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Osmotic Pressure

(*A* GENERAL DISCUSSION *held by the Faraday Society on Tuesday, May* 1, 1917,
SIR OLIVER LODGE, F.R.S., *in the Chair.*)

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The Faraday Society was founded in 1903 to promote the study of Pure and Applied Electrochemistry, Electrometallurgy, Physical Chemistry, and Metallography.

The subscription to the Society is £2 a year for Members, and £1 a year for Students. Members also pay an Entrance Fee of £1, with the exception of Members of the Chemical Society, the Institute of Metals, the Institution of Electrical Engineers, the Iron and Steel Institute, the Physical Society, and the American Electrochemical Society, who are admitted **without Entrance Fee** and without the usual formal nomination.

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Osmotic Pressure.

A General Discussion.

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OSMOTIC PRESSURE.

A GENERAL DISCUSSION.

At the meeting of the Faraday Society held on Tuesday, May 1, 1917, in the rooms of the Chemical Society, Burlington House, London, W., a **General Discussion** on **Osmotic Pressure** took place. The discussion was presided over by **Sir Oliver Lodge, F.R.S.**, who was introduced into the Chair by the **President, Sir Robert Hadfield, F.R.S.**

Sir Robert Hadfield : As your President, I am sure you will expect me to give a few words of welcome to Sir Oliver Lodge for taking the trouble to be with us this evening and occupying the Chair ; we know how busy he is and what a load of work he has upon his shoulders. His remarks on the many subjects with which he deals are always of the greatest interest, and I am sure those he will make this evening will be equally so.

With this subject of "Osmotic Pressure" I am but little acquainted, but I hope that some day its consideration will be found to have some bearing on problems of ferrous metallurgy. This is not at all improbable, as this and the colloid condition of matter have probably something to do with this particular branch of scientific knowledge.

I have never forgotten the most interesting experiments carried out by Dr. Acheson before this Society some years ago, and the excellent paper he read to us in which he showed that ordinary graphite in a dilute solution of tannin then became so attenuated that not even the finest filter paper was able to stop the passage through it of this modified graphite. The actual reagent used was a solution of gallotannic acid containing a little ammonia. This was found to render the graphite perfectly suspensive, so that it would pass through filter paper and obey all the laws of a colloidal solution. The reduction in size of the graphite particles on deflocculation was about $\frac{1}{1000}$th part of the particles that had been passed through a sieve having 40,000 meshes per square inch, and Dr. Acheson thought this really represented the molecule of carbon. This particular form of carbon may or may not exist in a combination of iron and carbon, known as carbide of iron. At any rate, I throw out the suggestion for consideration. This mysterious and remarkable carbide is of vital importance, and if it did not exist there would not be available in the world that wonderful material known as steel, upon which the progress of mankind depends.

With this introduction I now ask Sir Oliver Lodge to take the Chair.

INTRODUCTORY ADDRESS ON "OSMOTIC PRESSURE."*

BY SIR OLIVER LODGE, F.R.S.

Sir Oliver Lodge, in opening the discussion, said: Mr. President, Ladies, and Gentlemen,—I thank you for the welcome you have kindly given me. The President has really introduced the subject by the characteristic remark that there is nothing like steel, and I dare say, though it did not strike me before, that this subject is perhaps connected with some of the problems of the solution of carbon in metal. The laws of gases may perhaps apply to those particles of carbon.

The subject of osmosis is of vital importance in a very definite sense. It is important in animal and vegetable economy. The part that it plays in our own bodies must be very extensive; the part that it plays in vegetation is conspicuous. It has to account for the rise of sap in trees, for one thing; also, I do not know whether it has struck people how remarkable it is that fruits can retain their moisture by purely physical means in the tropical sunshine. Even the thin skin of a peach retains its moisture, in a way which no ordinary membrane without specific properties could possibly do; and we know from the investigations of Dr. Adrian Brown on barley that a semi-permeable membrane is of great importance in connection with grain.

The subject of osmosis has two sides, the practical and the theoretical, and the practical side leads us to biology. It is the theoretical side with which we are more occupied to-night. It depends essentially on molecular discrimination—discrimination between the different kinds of molecules; the kind of thing for which Maxwell invented his demons. Molecular discrimination is the essence of osmosis. One conspicuous form of molecular discrimination is evaporation. The substance that evaporates say from a salt and water is pure water, the solvent, not the dissolved substance: the dissolved substance or solute becomes concentrated as evaporation goes on. There you have a boundary acting as the discriminating agent—a sort of semi-permeable membrane, as G. F. FitzGerald pointed out. Another example of molecular discrimination is freezing. When you freeze a solution of salt and water the ice is purer, less salt, than the remainder of the liquid; hence in both cases you get concentration of the dissolved substance and discrimination at the boundary. With a semi-permeable membrane, whether natural or artificial, the same thing is conspicuously true. Hence all these processes must be governed to some extent by similar laws—the vapour tension, the boiling-point, and the osmotic pressure must all be connected—and we know by thermodynamic theory that they are.

One may treat the theory of osmosis thermodynamically, in a sort of blindfold manner, not attending to what is actually going on, but only to the results; or we may try to treat it in a molecular and kinetic manner, attending to what the molecules are doing. We may consider in what way the membrane acts; we may then try to find the reason for its action, and of course we must study the results of its action.

The best known molecular theory is the gas theory, treating the molecules of a dissolved substance in a solvent as if they were molecules of a gas in free space, or at least molecules of one gas jostling about among the molecules of another.

Lord Kelvin, I remember, expressed himself adversely to any attempt to apply gas theory to the very different conditions of a dissolved substance; but it is well known that the laws are singularly alike, whatever the reasons for that similarity may be. When the solution is very dilute, even the laws of a perfect gas fairly apply. As the solution becomes more concentrated, the more complicated but well-known gaseous laws must be used instead. Lord Kelvin would not allow that the molecules of a substance in the midst of a solution could be treated by the kinetic theory of gases, because the conditions were so entirely different. In the one case they are flying in a free space, and in the other they are crowded by other molecules; but whether he was right or not in denying the applicability of gas theory is doubtful. He was not always right in all his *obiter dicta*. He had an instinct for being right when he had studied a subject, but he sometimes gave his opinion when he had not, and occasionally he must have been wrong. It is only human.

It is noteworthy that the theory of gases has been applied even to the crowd of electrons inside a metal, the gaseous theory of electric conduction in metal. The presence of the President, however, reminds me that J. J. Thomson, in a remarkable paper read before the Institute of Metals, began to throw doubt upon this gaseous theory of metallic conduction, and to substitute an admirable one of his own—which at present, so far as I know, holds the field, though the subject doubtless requires much more exploration.

Another theory of osmosis makes it depend on the molecular attraction of cohesion, or what is called Laplace's K—the interaction of the molecules of the solvent with one another, and the interference with that interaction by the dissolved substance; so that the value of K is either increased or diminished, leaving a balance in either case which can be observed as the osmotic pressure, a pressure, that is, which has to be sustained by the semi-permeable and other walls of the vessel, instead of being controlled completely by the internal molecular forces.

And when we come to the subject of cohesion, that in itself requires explanation. I cannot but suppose that it is a kind of residual chemical affinity and must be explained electrically. There is an electrical theory of cohesion, or at least of the action of a boundary layer, in the *Philosophical Magazine* for April this year, by a Russian senior student named Frenkel, which, whether it holds water or not, is worthy of attention and is very ingenious. His theory depends on the structure of the astronomical atom; that is to say, the atom with a positive nucleus and electrons revolving in orbits depending on the inverse square of the distance. It is sometimes spoken of as the Rutherford atom, to distinguish it from the direct-distance law of action ingeniously worked out by J. J. Thomson; but it is not peculiar to Rutherford. I have heard Poynting advocate it long ago. And Sir Ernest Rutherford has done such an immense amount of fine work that one need not be excused for preferring a name such as "astronomical atom" rather than a name with a personal significance. Personal names attached to things are apt to become troublesome hereafter.

Now about the discussion to-night. I think Dr. Porter is applying gas theory to the dissolved substance, to the solute, treating the dissolved substance as obeying the laws of imperfect gases. I think Mr. Bousfield wishes rather to apply gas theory to the solvent, i.e. to the liquid which holds and actively dominates the solute. And then Dr. Tinker appears to deal with the matter on a cohesion or adsorption basis, attending chiefly to the membrane and its properties. Hence we shall have, I think, three different views put before us. Now, we have met for the purpose of discussion, and not so much for hearing three papers which have been circulated; hence if we are going to have discussion we have not time to read the papers through. I think the authors of the papers will agree that it would be a mistake to burke discussion by excessive reading of the papers. I suggest, therefore, to the readers of the papers, from the point of view of discussion, to do what the Royal Society often does—take the papers which have been circulated as read and concentrate on some specific points. I suppose the authors of the papers will have read each other's papers and will perceive points that want emphasis, points which are capable of discussion; and will be able thereby to give some chance of arriving at a clear difference of opinion, or perhaps some more agreement than that with which we start. At present, I do not see a clear agreement between these papers, and that is all the better; the great point is to get our ideas and differences clearly marked. May I therefore venture to suggest that a certain amount of brevity and at any rate a certain amount of concentration on specific points will be desirable? I now have great pleasure in calling upon Dr. Porter to open the discussion.

THE KINETIC THEORY OF OSMOTIC PRESSURE.

Professor Alfred W. Porter, D.Sc., F.R.S., presented the following Paper on "The Kinetic Theory of Osmotic Pressure":—

It is not my intention to summarize the present state of our knowledge in regard to osmotic pressure. It is not many years since a discussion on the subject took place in this Society (January 29, 1907), in the course of which some account was given of the state of experimental knowledge at that time and of theoretical explanations of the experimental facts. Since that time there has been a considerable amount of work done both on the experimental and the theoretical side, and this must claim our attention. Quite a large part of this is free from any disputatious matter; especially the part which rests upon thermodynamical relations. On the other hand, when we turn to the causes of osmotic pressure, no unanimity is yet to be found, and on this point I have some remarks to make. Again, no full examination has yet been made of Morse and Frazer's experimental results; these, also, claim one's attention.

As the term osmotic pressure does not possess an invariable meaning, it is necessary to state that I shall always mean by it *the equilibrium difference of pressure between a solution and the pure solvent when separated by a membrane permeable to the solvent alone.* In any solution the masses of solvent and solute will be denoted by M and m and the corresponding numbers of molecules by N and n.

The Kinetic Theory of Osmotic Pressure.

I consider first the kinetic theory of osmotic pressure. It is better to speak of kinetic theory than gas theory, because the latter term is often taken to imply conformity with the laws of *perfect* gases. No upholder of the theory has ever supposed that the perfect gas laws for osmotic pressure would hold good in all cases; but that they would be approximated to in the case of dilute solutions only. On the other hand, opponents of the theory have made the most of the fact that strong solutions exhibit great deviations from those laws. These deviations, of course, no more militate against the kinetic theory than do analogous deviations in the case of gases themselves. The greatest triumphs of the kinetic theory have been obtained (by Hirn, van der Waals, Dieterici, and others) in, at least partially, accounting for the complexities in the behaviour of gases. Yet similar complications in the case of osmosis are frequently supposed to be fatal to the theory. In spite of the fact that this theory is the *only one* which directly gives the experimentally obtained values for dilute solutions, it has met with great opposition both from physicists and from certain schools of chemists. The strength on the side of the opponents lies in a recognition of the fact that the conditions in a liquid are certainly not *identical* in every respect with those in which the molecules of a gas move. However, our knowledge in regard to liquids has increased extensively in the last few years. There is now an experimental basis for a kinetic theory of liquids supplied by the investigations of Perrin and others on Brownian motion. Particles suspended in a liquid are in rapid motion to the precise amount required by theory. This statement must apply to the molecules of a solute also; and the dynamical effect of this motion must needs be taken into account. This effect, calculated according to legitimate methods, comes out equal to the experimental value of osmotic pressure. Any other theory put forward to account for osmosis must fulfil, then, a double duty: not only must it be competent to explain osmosis, but it must also explain *away* the effects that we have the right to expect from the molecular agitation of the solute.

The curious objection is often raised that the pressure according to the kinetic theory of gases goes the wrong way. This objection would hardly deserve notice if it were not for its extreme vitality. A controversy has recently taken place between van Laar and Ehrenfest * on this point; it is reported in *Nature* for March 16, 1916.

In van Laar's opinion the pressure of the sugar molecules against the semi-permeable membranes would drive the water out.

The consideration of the subject is usually complicated unnecessarily by endeavouring to deal at the outset with real molecules occupying space and attracting and attracted by all other molecules present. Warning should be taken from the difficulties which arise in the kinetic theory of gases when this thoroughgoing procedure is adopted. It is better to suppose the solute to consist of moving massive points; for then its introduction into a solvent does not displace the molecules of the latter. Much of the difficulty is thereby removed.

Consider a long vessel of water under uniform pressure throughout. In the left hand half disperse a number of ideal sugar molecules so as to form a dilute solution. If left alone they will slowly diffuse throughout the water. The rate of diffusion will, of course, depend upon the viscosity of the water; but this rate does not concern us. In order to prevent diffusion a force from right to left must be introduced, acting only upon the sugar. It does not matter how this force is introduced. A row of demons, clinging to fixed supports, would serve—each with instructions to keep the sugar molecules from getting through. These demons require to exert no force so far as the water is concerned, because it presses upon them equally on all sides.

The pressure of the sugar arises from its thermal motion; and Perrin has given evidence that this is the same as for a gas. The reversal of this motion at the screen requires the same pressure as for the corresponding case of a gas. This is the osmotic pressure. The sides of the vessel (or any body immersed in the solution) experience pressure due both to sugar and water; and therefore equilibrium exists with a difference of pressure between the two sides of the semi-permeable screen, the balance being taken up by the screen.

In order to obtain a picture of the principal effect of the presence of a solute we may regard it as helping, by its molecular bombardment, to enlarge the boundaries of the solution, and thereby to relieve the total pressure on the solvent. If the solution be now put into communication with the solvent at the same external pressure, the latter flows in. This process has recently been called osmotic suction, and perhaps this name describes it well enough, though I doubt if "suction" is a scientific word.

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* Ehrenfest, *Proc. Amsterdam Acad.*, xvii. pp. 1241–45; J. J. van Laar, ibid., xviii. pp. 184–90.

But it must be remembered that, however interesting the processes concerned with the flow of the solvent may be, the quantity which we call the osmotic pressure is concerned primarily with the equilibrium state; it is an outwardly directed pressure upon the semi-permeable membrane, and it is given in amount by the bombardment pressure of the solute against that membrane—at least in the case of dilute solutions.

Of course, when the solvent and solute are *both* gaseous the *modus operandi* (as sketched above) is, I believe, admitted by all. Hot silica is permeable to hydrogen, but not to nitrogen; and it constitutes, therefore, a selective membrane. Let a cylinder, with piston, have such a membrane fitted to it; and, when containing nitrogen, immerse it in hydrogen. Hydrogen enters, and the vessel expands, unless additional pressure is exerted upon the piston. In this case the total pressure that will keep the volume unchanged is the sum of the pressures of the two gases. Attractive forces, surface tension, etc., have nothing to say to it, because these forces do not exist.

These statements, applied to liquids, require that the solution shall be very dilute. In such cases the aggregates, of which the molecules of the solute are the centres, are so far apart from one another that further dilution of the solution will merely separate them without interfering with the constitution of any of them. The change of mechanical energy which arises from further dilution is then independent of the kind of matter involved, and will depend only upon the number of such aggregates and be the same for all systems which agree in this respect. "One such system is an ideal gas, there being now no solvent; it follows that the osmotic pressure of the molecules of the dissolved substance against an internal partition, permeable to the solvent and not to them, is the same as if they existed in the state of an ideal gas at their actual density and temperature." *

This equality can be proved also by means of a thermodynamical cycle, such as that made use of by Lord Rayleigh; † but, of course, any such proof gives no hint of the mechanism by which the equality is brought about.

It will be seen that I find it impossible to put myself in the mental position of FitzGerald in his Helmholtz Lecture ‡ (which is one of the most noteworthy contributions to the cult of caution in the advocacy of scientific theories). He says: "It is no doubt a most remarkable thing that osmotic pressure should be even roughly the same as what would be produced by the molecules of the body in solution as if in the gaseous state; but to imply that the dynamical theory of the two is at all the same, or that the dynamical theory of a gas is in any sense an *explanation* of this law of osmotic pressure is not at all in accordance with what is generally meant by the word 'explanation.'" I wish to dissociate myself completely from the position adopted in this sentence.

Of course, when the processes by which the final equilibrium state are set up or the properties of the membrane which make it semi-permeable are examined, many interesting connections will certainly be found which will make it possible to express osmotic pressure in terms of them. It is often difficult to distinguish between cause and effect in the case of concomitant events. The kinetic pressure of the solute acts outwardly and diminishes the Laplacian pressure by an equivalent amount, and therefore connections may be found between osmotic pressure and Laplacian pressure. But the prime-mover, or *causa causans*, of the whole disturbance seems indubitably to be the molecular agitation of the solute, and a knowledge of this provides us with *the only way in which the value of the pressure has been calculated from theory.*

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* Larmor, *Æther and Matter*, p. 287.

† *Nature*, lv. p. 253 (1897).

‡ *Trans. Chem. Soc.*, 1896.

In concentrated solutions it is unwarrantable to neglect the attractive forces and volume of the solute molecules; and indeed they may become the most important factor. To recognize this is in no way to give up the gas theory; unless, indeed, it is claimed that van der Waals gave up the theory for gases themselves when he wrote his famous treatise on the continuity of the liquid and gaseous states. Nor must it be expected that the equation for osmotic pressure will be identical with the characteristic equation of a simple gas. In the osmotic problem we are dealing with, at least, a binary mixture. This is a type of problem which has been tackled by the Dutch school of physicists; but it is not surprising that their efforts at present are only tentative. The true characteristic equation for a *simple* fluid is not yet known; the problem of the binary mixture is a much harder one.

The Semi-permeable Membrane.

The properties of the membrane form an interesting and important but quite subsidiary problem. Provided it is truly semi-permeable, the value of the difference of pressure between its two sides is determined by the properties of the solution and solvent and not by those of the membrane. Its semi-permeability, no doubt, must be expressible in terms of its own properties. It has to exert a pressure which is equal to the aggregate of the forces required to stop the solute while affording a passage for the solvent. In order to act as such a membrane, any canals through which fluid can permeate must be narrow compared with the range of molecular forces. So long as this is the case there seems to be nothing to prevent them being so narrow that the passage of the solvent through them can be described as a process of *solution* in the material of the membrane; or at least of that coarser kind of solution which is distinguished as colloidal. But it does not appear true that semi-permeability always arises in this way. The most perfectly semi-permeable membrane known (as FitzGerald pointed out) is the surface of separation between a solution and its vapour. Here, the sorting is effected in the Laplacian layer, which exerts such attraction on the sugar that it practically never succeeds in escaping through. Where solubility is the determining factor a study of the membrane will bring out the influence of the properties concerned with a variation of solubility and may throw light upon the nature of solutions. These, however, are collateral studies and have no more connection with osmotic pressure than the study of the elastic properties of a glass vessel has upon the origin of the pressure it experiences from the water contained in it.

An Interpretation of Experimental Results.

Experimental advance since 1907 has been made mainly by Morse and his collaborators in America and by the Earl of Berkeley and his co-workers in Britain. To Lord Berkeley we owe observations extending over the widest range of concentrations at one temperature only; to Morse we are indebted for a set extending over a fair range of concentrations but at various temperatures between 0° C. and 80° C. Lord Berkeley's values for cane sugar are given in Table I, together with values calculated according to the perfect gas law and Morse's values at 0° for comparison.

Cane Sugar. Temp. 0° C.

Wt. Norm. Conc. $1{,}000\,\frac{n}{M}$ (approx.).	Weight Conc. $100\,\frac{m}{M}$.	Volume Conc. $c\,\frac{\text{grams}}{\text{litre}}$.	Osmotic Pressures.		
			Berkeley and Hartley. Observed.*	Calculated. $PV = nRT$.	Morse. Observed.
·1	3·3927	32·6	2·23 atm.	2·13	2·43
·3	10·184	90·1	6·85	6·2	7·02
·6	20·525	176·8	14·21	12·0	14·38
·9	30·608	256·7	21·87	18·0	21·92
1·0	33·945	—	24·55	—	24·57
2·39	81·262	540·6	67·74	40·5	—
3·29	111·731	659·6	100·13	46·0	—
4·1	141·107	751·4	134·84	52·8	—

It will be seen that there is some disagreement between the two experimentalists; the discrepancy has not yet been explained. Both sets are in excess of the perfect-gas pressures even for the most dilute solutions.†

Morse's values have the most importance for us, because they cover a wide range of temperature. They are given in the Table ‡:—

OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS.

Weight-normal Concentration.

Mean Osmotic Pressure in Atmospheres.

Temp.	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
0°	(2·462)	4·722	7·085	9·442	11·895	14·381	16·886	19·476	22·118	24·825
5°	2·452	4·818	7·198	9·608	12·100	14·605	17·206	19·822	22·478	25·283
10°	2·498	4·893	7·334	9·790	12·297	14·855	17·503	20·161	22·884	25·693
15°	2·541	4·985	7·476	9·949	12·549	15·144	17·815	20·535	23·305	26·189
20°	2·590	5·064	7·605	10·137	12·748	15·388	18·128	20·905	23·717	26·638
25°	2·634	5·148	7·729	10·296	12·943	15·624	18·434	21·252	24·120	27·053
30°	2·474	5·044	7·647	10·295	12·978	15·713	18·499	21·375	24·226	27·223
40°	2·560	5·163	7·844	10·599	13·355	16·146	18·932	21·803	24·735	27·701
50°	2·635	5·278	7·974	10·724	13·504	16·319	19·202	22·116	25·123	28·213
60°	2·717	5·437	8·140	10·866	13 666	16·535	19·404	22·327	25·266	28·367
70°	—	—	—	—	13·991	16·820	19·568	22·567	25·562	28·624
80°	—	—	—	—	—	—	—	23·062	25·919	28·818§
90°	—	—	—	—	—	—	—	—	—	—
100°	—	—	—	—	—	—	—	—	—	—

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* Berkeley and Hartley, *Proc. Roy. Soc.*, A, 92, p. 483 (1916).

† A suggested explanation of this has been given by G. N. Lewis, *J. of Amer. Chem. Soc.*, vol. xxx., No. 5, May 1908.

‡ Morse, Holland, Myers, Cash, and Zinn, *Amer. Chem. J.*, 48, 29 (1912).

§ The last value in the table is given as 28·000 by Morse and also (by quotation) by other writers. A comparison with Morse's detailed table shows that it should be 28·818.

Morse exhibits the deviations from a fictitious gas law by calculating the ratios of these numbers to the values of the pressures of a gas containing the same numbers of molecules in a volume equal to the volume (not of the solution but) of the pure solvent at 4° C. This process is so arbitrary that it leaves one with a very vague sense of what his ratios signify. I therefore do not quote them.

In a letter to Lord Berkeley about eight years ago I showed that his values could be calculated approximately from a formula of Hirn's type—

$$P(v - b) = RT,$$

where b is a constant not much different from the volume of sugar present. He did not think that the formula did complete justice to the accuracy of his experiments, and I am inclined to agree with him. To show the capability of this formula of giving a second approximation, I append a table in which it is applied to Morse's values at 20° C. and in which b is taken as ·310 litres/mol.

Weight Normal Concentration. $1{,}000\frac{n}{M}$.	Volume Normal Concentration. $c\,\frac{\text{grammol.}}{\text{litre}}$.	Osmotic Pressure.	
		Observed.	Calculated.*
·1	·098	2·59	2·43
·2	·192	5·06	4·91
·3	·282	7·61	7·43
·4	·369	10·14	10·02
·5	·452	12·75	12·64
·6	·533	15·39	15·35
·7	·610	18·13	18·09
·8	·684	20·91	20·87
·9	·756	23·72	23·74
1·0	·825	26·64	26·64

The agreement at high concentrations is excellent; but is not so good for the more dilute solutions. The volume of a gram molecule of solid sugar is about ·214 litre. The high value ·310 which is required might be accounted for by assuming that the sugar is hydrated in solution, the difference, 0·96 litre, representing the water of hydration. This would correspond to 96/18 or 5·3 molecules of water associated with each molecule of sugar on the average. Callendar had previously found by a different line of argument the value 5 from Berkeley's numbers.

It is necessary, however, to examine all of Morse's numbers, and instead of assuming a constant value of b for each temperature it is better to work backwards and find the value of b for each concentration and temperature which would make the Hirn equation correct; and thence to determine the hydration number for each case. These are given on the opposite page.

Only the values up to 60° C. are given, because no table is available of the densities of sugar solutions at higher temperatures; and these densities are needed in calculating the table.

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* From formula $P(1 - \cdot310c) = cR293$.

HYDRATION NUMBERS.

Wt. Conc.	0°.	10°.	20°.	30°.	40°.	50°.	60°.
·1	53	43	45	3	6·9	8·8	11·5
·2	15·8	16	16	7	5·5	4·5	5·8
·3	10·3	10·3	11·2	6·7	6·0	4·1	3·5
·4	7·7	8·0	8·3	6·3	6·4	4·3	2·8
·5	6·9	6·8	7·2	6·0	6·0	4·3	3·0
·6	6·4	6·3	6·5	5·7	5·7	4·3	3·2
·7	5·9	6·0	6·3	5·6	5·2	4·3	3·2
·8	5·7	5·7	6·5	5·6	5·0	4·2	3·3
·9	5·5	5·5	5·8	5·4	5·0	4·4	3·3
1·0	5·5	5·5	5·8	5·4	4·9	4·5	3·6

For comparison, the values calculated in the same way from Berkeley's determinations are appended :—

Wt. mol. conc.	·1	·3	·6	·9	2·39	3·29	4·1
Volume conc. grams per litre	32·6	90·1	176·8	256·7	540·6	659·6	751·4
Hydration number ...	14	17·6	8·0	5·3	4·8	4·4	4·0
Mol. of water present per mol. sugar	550	183	82	61	24	16·5	13·4

Both sets agree in giving diminishing hydration with increasing concentration. In other respects, the agreement is not too close; but it must be remembered that in dilute solutions in particular the degree of hydration has an exceedingly small influence on the pressure.

The values obtained for dilute solutions at low temperatures seem surprisingly large; but I am not aware of any argument which makes them impossible. If we represent the volumes of sugar and water molecules by their representative spheres these will have radii in the ratio of 6 to 2·6. Between 30 and 40 molecules of water would form a single layer on a sugar molecule. (The actual number would depend upon the nature of the packing.)

Now, it is exceedingly probable that the molecules of water immediately contiguous to each sugar molecule tend to form a condensed layer round it. No doubt this association, as in all other cases of molecular equilibrium, is only a kinetic one; these layers will continually be breaking up and re-forming. The hydration that can be found experimentally will represent an average or statistical value of the number of molecules in the condensed layer. Thus the values obtained from Berkeley's numbers come well within the range of probability. As the amount of water present per each molecule of sugar becomes less, the hydration becomes less, as we should expect it to do. In the strongest solutions used by Morse there are about 55 molecules of water present per molecule of sugar. Hence, in this case about one-tenth of the total amount forms the condensed or associated layer. In the strongest solutions employed by Berkeley there are 13·4 molecules of water present and 4 in the condensed layer—in each case per molecule of sugar.

I see nothing in these results to indicate the degree of association of the water molecules with each other—mono-, di-, trihydrol are indistinguishable.

Perhaps other contributors to this discussion will have evidence to bring forward bearing upon this side of the question.

Callendar in 1908* came to the conclusion that the sugar molecules are hydrated in solution from a quite different line of reasoning. He modified a theory due to Poynting,† and assumed that the ratio of the saturation vapour pressures of solution and pure solvent (π_π/π_0) is "equal to the ratio of the number of free molecules of solvent to the whole number of molecules in the solution, instead of to the number of molecules of solvent. If each molecule of solute appropriates a molecules of solvent and if n, N denote, as before, the whole number of molecules of solute and solvent respectively in the solution, the number of free molecules of solvent is $N - an$ and the whole number of molecules in solution is $N - an + n$." He thus obtains

$$\frac{\pi}{\pi_0} = \frac{N - an}{N - an + n}$$

or

$$\frac{\pi_0 - \pi}{\pi} = \frac{n}{N - an}.$$

According to the classical formula for dilute solutions $a = 0$; according to Poynting's theory $a = 1$; Callendar finds for cane sugar the value 5 from various physicochemical properties; but for high concentrations as determined from boiling-points near 100° C. he finds it to diminish gradually to 3.‡

Apart from the somewhat arbitrary character of the above formula for the lowering of vapour pressure there is an essential difficulty in connection with it which requires further discussion. According to van't Hoff's original formula, obtained thermodynamically,

$$\frac{\pi_0 - \pi}{\pi} = \frac{n}{N}.$$

N is explicitly the number of molecules of the solvent *estimated of the same degree of complexity as in the vapour phase.* In fact, it is a convenient abbreviation for M/μ, where M is the mass of solvent and μ is the molecular weight of water *vapour.* The number of real molecules of the solvent liquid does not primarily enter into the problem at all. Now, water is believed to be associated, and therefore N is not the number of water molecules present even if hydration is neglected. I am puzzled therefore in endeavouring to understand in what sense $N - an + n$ is taken to be the total number of molecules present. This objection seems to strike at the very foundation both of Poynting's assumption and of Callendar's modification of it. There may be a way out of the difficulty, but the mode of escape has not yet been discussed or even hinted at.

On the totally different hypothesis which underlies the calculations of hydration in the present Paper, I have shown§ that the formula for the lowering can be written approximately

$$\log\frac{\pi_0}{\pi} = \frac{n}{N - an}$$

in which N is explicitly the number of molecules of water reckoned as if normal and not the number of actual molecules present.

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* *Roy. Soc. Proc.*, A, vol. 80, p. 482 (1908).

† *Phil. Mag.*, vol. 42, p. 298 (1896).

‡ It is noteworthy that, according to Poynting's theory, the osmotic pressure should be increased in the ratio a when a differs from unity. A discordance would arise in this connection; for no such increase is observed.

§ *Trans. Faraday Soc.*, vol. xi, part 1, p. 27, 1915.

Latent Heats of Dilution.

A test of the value of Morse's determinations can be made by aid of a knowledge of latent heats of dilution. I observe in a Paper contributed to this Society* that the latent heat is connected with osmotic pressure by the following *nearly* exact equation :—

$$H_i\dagger = sT^2\frac{\partial}{\partial T}\left(\frac{P}{T}\right)$$

Since for a perfect gas P/T is independent of temperature, the latent heat of dilution would be zero if the osmotic pressure followed exactly that law. The value of H_i gives, therefore, a measure of the degree of departure from the law of perfect gases so far as change of temperature is concerned. Not many values of this quantity are yet known. For sugar there are a few determined by Stackelberg. Mr. Orson Wood, M.Sc., has recently determined some more at 20° C. at my suggestion, and I am able to quote some previously unpublished results. The values obtained by him have been determined with very great care, and it is interesting to know that they lie on a curve passing through Stackelberg's points, so that both sets confirm one another. In the following table I give these values for certain concentrations, together with the values of $y = \frac{\partial}{\partial T}\left(\frac{P}{T}\right)$ calculated from them and from Morse's values at 10° C. and 30° by assuming y to be uniform between those temperatures.

$1{,}000\,\frac{n}{M}$.	H_i cal./gram.	y calculated from H_i.	Calculated from Morse's Observations.
·5	— ·04	— ·000019	— ·000031
·8	— ·07	— ·0000339	— ·0000338
·9	— ·09	— ·000044	— ·000044
1·0	— ·11	— ·0000537	— ·000047
1·5	— ·245	— ·00012	—
2·0	— ·415	— ·00020	—
4·0	— 1·12	— ·00055	—

The correspondence between the values of y calculated in the two ways is not exact; but the values are of the right order. It must not be thought, however, that the whole of Morse's determinations will stand the application of this test; it is far too searching. This can be seen even by a casual examination of an entire table of values of P/T calculated from his numbers. Nor are these latent heats known at other temperatures. These are being obtained by Mr. D. O. Wood, and will constitute an important check upon determinations of osmotic pressure. In fact, in my opinion, values of osmotic pressures calculated from heats of dilution and from a standard set at some most convenient temperature (say 0° C.) may be considerably more accurate than those determined directly.

Some light can be thrown on the possible physical meaning of the existence of a latent heat by considering what the value of $T^2 \frac{\partial}{\partial T}\left(\frac{P}{T}\right)$ is according to van der Waals' equation. If in the equation

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* *Trans. Faraday Soc.*, vol. xi, part 1, p. 22, 1915.

† The value H_i is strictly the internal latent heat of dilution, but it is very nearly identical with the latent heat due to ordinary mixing.

$$(P + K)(v - b) = RT,$$

K and T be assumed independent of temperature,

$$T^2 \frac{\partial}{\partial T}\left(\frac{P}{T}\right) = K,$$

and this would require K to be negative, which, in my opinion, is exceedingly unlikely to be the case, although the possibility of it has been entertained. However, it is now admitted that K is a function of temperature, and therefore

$$\frac{\partial}{\partial T}\left(\frac{P}{T}\right) = -\frac{\partial}{\partial T}\left(\frac{K}{T}\right);$$

or, if P increase less fast than the absolute temperature, K increases faster than it. This is not at all impossible.

According to the view which has been dealt with in this Paper in detail, it is b that is a function of temperature; and K has been ignored. This gives

$$\frac{\partial}{\partial T}\left(\frac{P}{T}\right) = \frac{R}{(v - b)^2}\frac{\partial b}{\partial T},$$

and the negative value of the left-hand side signifies that b diminishes with temperature rise. My reason for ignoring K is that if it is taken into account b must be even larger than the numbers I have given. It is difficult to discriminate between the above alternatives; all of them are equally consistent with the observed heats of dilution. In the case of dilute gases for which b is small compared with v,

$$p + K = \frac{RT}{v}\left(1 + \frac{b}{v} + \quad\right),$$

and we may write $p = AT + B$ where the effects arising from K and b are merged in the single term B. This indicates still further the difficulty of distinguishing between them.

Solubility.

The variation of the solubility of cane sugar with temperature can be accounted for in the main by assuming that it is due to the release of the water of hydration. The values of hydration numbers, for saturated solutions, that would be required if the variation were wholly due to this cause are given under the heading *a* below:

Temp. C.	0°	20°	40°	60°	80°
a	6·9	5·7	4·7	3·0	1·6

THE COLLOIDAL MEMBRANE: ITS PROPERTIES AND ITS FUNCTION IN THE OSMOTIC SYSTEM.

Sir Oliver Lodge: Dr. Porter has told us that the dissolved substance is everything that matters, and he has also brought in a very interesting remark on molecular aggregates, which I expect Professor Armstrong will have something to say about later on. Dr. Tinker is going to tell us, I expect, that the membrane is everything that matters.

Dr. Frank Tinker (University of Birmingham) then read his Paper on "The Colloidal Membrane: its Properties and its Function in the Osmotic System."

During recent years the thermodynamic theory of osmosis has undergone considerable development at the hands of several mathematicians and physicists, who have shown that the osmotic pressure of a solution is a somewhat complex function of such diverse factors as the vapour pressures, specific volumes, coefficients of compressibility, heats of dilution, etc., of both the solution itself and of the pure solvent also.* On the other hand, the kinetic side of the subject has remained more or less stationary, the majority of the theories purporting to explain the mechanism of osmosis having little to say with respect to how and why osmotic pressure is dependent on almost all the other physical properties of solutions. Inasmuch as the subject is evidently too complicated for *a priori* hypotheses, it seems desirable that we should study exhaustively all the parts which go to make up an osmotic system. More particularly, in addition to considering the properties of the pure solvent and solution themselves, we should include the membrane—its structure, properties, and behaviour to the solvent and solute respectively; and the conditions governing osmotic diffusion across it.

The common colloidal membranes of the copper-ferrocyanide type are built up by the aggregation of small colloidal particles ranging in diameter from 50 to 400 $\mu\mu$.† The interstices between these particles form the pores of the membrane, the average capillary diameter being of the order of from 10 to 20 $\mu\mu$. Although the pore diameter is relatively great as compared with the diameter of the ordinary crystalloidal molecule, it is small enough for the whole of each capillary to be entirely under the influence of surface phenomena; and when osmotic flow takes place, say from a pure solvent to a solution, the moisture which diffuses is temporarily in the adsorbed or superficially condensed condition for such time as it is in contact with the membrane. Moreover, the adsorption effects shown by colloidal membranes are selective in nature; a copper-ferrocyanide film, for instance, taking up water rather than cane sugar from aqueous solutions of the latter,‡ thus explaining why this membrane is permeable to water but not to sugar. If the membrane is of a neutral nature, as is the case with the inner sheath of the skins enclosing barley seeds, its behaviour to the solute follows closely the lines laid down by the well-known Gibbs-Thomson rule. The vegetable membrane just indicated adsorbs and is highly permeable to solutes such as the phenols, amines, and fatty acids, which give solutions having a low surface tension; whilst on the other hand it is impermeable to the sugars, polyhydric alcohols, most inorganic salts, and other solutes whose solutions have high surface tensions.[*] Evidently the property of selective permeability which such membranes possess is a direct consequence of the selective adsorption effects shown by the colloidal particles composing the membrane.

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* See, for instance, the work of Porter, Trevor, G. N. Lewis, Bancroft, van Laar, and others.

† Tinker, *Proc. Roy. Soc.*, A, vol. 92, 357 (1916).

‡ Idem, ibid., A, 1917 (contemporary number).

With regard to the cause for osmotic flow, the fact of fundamental importance is that a colloid usually absorbs more moisture from pure water than it does from an aqueous solution. Whereas, for example, 100 grams of dry colloidal copper-ferrocyanide imbibes about 30 grams of moisture from pure water, the same amount of colloid takes up only 13 or 14 grams of moisture from a 60 per cent. sugar solution.[†] An immediate deduction from this fact is that the side of a membrane in contact with a pure solvent has a greater moisture content than the side adjacent to a solution. Consequently diffusion of the solvent from one side of the membrane to the other takes place of necessity, owing to the impossibility of establishing equilibrium when the moisture content of the colloid is not uniform throughout. In other words, osmotic flow takes place because the pure solvent induces a greater pressure and concentration of moisture inside the membrane than the solution does. To prevent osmotic diffusion, a hydrostatic pressure must be applied to the solution. Provided the pressure is placed on the solution only and not on the membrane as well, the application of the pressure increases the amount of moisture taken up by that part of the colloid in contact with the solution; and when a hydrostatic pressure equal to the osmotic pressure is placed on the solution, the moisture pressure and concentration throughout the membrane becomes uniform, osmotic flow then ceasing.[‡] In many respects osmotic diffusion is thus very similar in nature to the process of vapour distillation. As is well known, the vapour pressure and concentration is usually greater above the pure solvent than it is above the solution. Application of a hydrostatic pressure to a solution raises its vapour pressure,[§] and when the applied pressure is equal to the osmotic pressure, the vapour pressures of the pure solvent and solution become equal to one another, the vapour distillation no longer proceeding in consequence. But although the two processes of osmotic flow and vapour distillation are essentially similar in character [||]—both being diffusion phenomena—they are by no means identical. In particular, the moisture inside the pores of a membrane is in a very much more concentrated condition than it is inside the vapour phase proper, owing to the fact that it is condensed on the surfaces of the colloidal particles composing the membrane. In the case of water the membrane concentration would appear to be about 20,000 times as great as the concentration of water vapour proper.

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[*] A. J. Brown and F. Tinker, *Proc. Roy. Soc.*, B, vol. 89, 373 (1916). The general osmotic properties of barley seeds have been discovered and studied by Professor A. J. Brown.

[†] Tinker, *Proc. Roy. Soc.*, A (contemporary number).

[‡] Some unpublished work by Professor A. J. Brown and myself indicates that if the pressure is placed on the membrane *as well as* on the solution, the amount of moisture taken up by the colloid does not increase.

[§] Sir J. J. Thomson, *Application of Dynamics*, p. 171; A. W. Porter, *Proc. Roy. Soc.*, A, 79, 319 (1907).

[||] A further important similarity is brought out when we consider the high temperature coefficient of the rate at which osmotic diffusion takes place. (Earl of Berkeley and E. G. J. Hartley, *Proc. Roy. Soc.*, A, 82, 271 (1909).) It is highly probable that the rate of osmotic diffusion is an exponential function of the temperature having almost the same exponential constant as the ordinary vapour pressure-temperature curves.

The analogy just indicated is, however, a very useful one. By means of it we can arrive at the reason for many of the anomalies met with in the phenomena of osmotic flow and osmotic pressure. The above justification of its use indicates that, for purposes of discussion and mathematical treatment, we can replace the actual membrane by a vacuum ; except, of course, when considering those quantities, such as the *rate* of osmotic flow, whose magnitude is determined wholly or in part by the actual nature of the membrane—that is, we can regard a vacuum as a particular kind of membrane * by the aid of which, on account of the relatively simple laws obeyed by vapours proper, we can arrive at the various factors governing the direction and power of osmotic flow, and the magnitude of the osmotic pressure which a particular solution can generate.

In this connection let us take first the case of osmotic flow between two solutions on which no external hydrostatic pressures are imposed. The direction of osmotic diffusion will be from the solution which generates the greater vapour pressure.† Inasmuch as the vapour pressure of a solution depends partly on its concentration and partly on other factors, such as the volume change which the solvent undergoes during the process of dissolving the solute in it, the heat of dilution, the formation of hydrates in certain cases, etc., all these factors have a hand in determining the direction and power of osmotic flow. The main factor is usually the relative molecular concentrations of the two solutions ; with the exception of heat of dilution, the effect on vapour pressure of the other factors is usually negligible ; at least this is so in the case of dilute and moderately strong solutions. If, however, we eliminate the concentration factor by working with two solutions having equal molecular strengths on opposite sides of the membrane, the direction of flow will be towards the solution which has the greater heat of dilution, since a positive heat of dilution tends to make the vapour pressure of a solution abnormally low.‡ In addition, since a solution which has a positive heat of dilution and abnormally low vapour pressure has also a high intrinsic pressure and surface tension,§ the direction of osmotic flow is likewise towards the solution which has the higher intrinsic pressure and surface tension. Herein comes the application of Traube's surface tension theory of osmosis. When limited as above to the case of osmotic flow between two solutions of approximately equal molecular strength, this theory is of considerable value in predicting under what conditions osmotic flow will be abnormal. It will be seen, however, that the surface tension theory only comes in when we are dealing with non-ideal solutions ; || nevertheless its

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* Impermeable, of course, to non-volatile solutes, but permeable to volatile ones.

† I.e. the greater *partial* vapour pressure of the solvent.

‡ If, of course, both solutions are ideal, having zero heats of dilution and equal surface tensions, etc., there will be no osmotic flow between them, provided that they are equally strong molecularly.

§ F. P. Worley has written an excellent experimental paper on the relation between surface tension and vapour pressure (*Jour. Chem. Soc.*, i., p. 273 (1914). In this connection see also a paper by myself (*Phil. Mag.*, September 1916).

|| An ideal solution is one whose vapour pressure is given in terms of the vapour pressure of the pure solvent and its own concentration by Raoult's relation—
$p' = \frac{N}{N + n}p.$

scope of application would appear to be very extensive, since most actual solutions deviate from Raoult's law and are in consequence more or less non-ideal.

Consider next the factors determining the magnitude of the osmotic pressure of a solution. The central fact in this connection is the simultaneous increase of vapour pressure with the application of hydrostatic pressure. It is evident that we can define the osmotic pressure as the hydrostatic pressure which, when applied to the solution, raises the vapour pressure of the latter up to that of the pure solvent. Taking this definition as a basis, it is quite a simple matter to deduce directly the well-known formula connecting osmotic pressure with vapour pressure, without resorting to the somewhat cumbrous method of the thermodynamic cycle.[*] It would appear also that, for dilute and moderately strong solutions at any rate, all the abnormalities in osmotic pressure owe their origin to abnormalities in vapour pressure.[†] Consequently many of the factors which tend to upset the simplicity of the laws of osmotic diffusion tend also to make osmotic pressures abnormal. In particular it is clear that if the vapour pressure of a solution under atmospheric pressure is abnormally low, its osmotic pressure will be abnormally high; the difference between its vapour pressure and that of the pure solvent, which has to be nullified by the application of a hydrostatic pressure to the solution before osmotic equilibrium can be attained, is greater than Raoult's law would require it to be. Consequently also the osmotic pressure is unduly high when the solution has a positive heat of dilution,[‡] or when it has a high intrinsic pressure and surface tension.

The problem as to *why* the vapour pressure of a solution, and indirectly therefore the osmotic pressure also, should be related to its concentration, heat of dilution, surface tension, etc., is a much more fundamental and difficult one than the question just treated as to *how* these properties are related to one another. It will depend for its complete solution on the accumulation of much more knowledge appertaining to the liquid state than we possess at present. My personal opinion with regard to this question is that the change in vapour pressure which the process of solution entails is largely the result of simultaneous changes which are purely physical in nature. When a solute is added to a pure solvent, the internal or thermal pressure of the latter *inside* the liquid is generally diminished, on account of the increase in volume and "free space" which accompanies the addition of the solute. If the pressure of the solvent within the liquid phase is thus diminished by the process of solution, it will likewise be diminished in the vapour phase without the liquid.[§] On the other hand, it would appear that chemical effects such as the formation of hydrates or solvates only cause disturbances in the magnitude of the vapour pressure. Associated solvents perhaps excepted, it does not seem likely that such effects are pronounced enough to make them into the primary factors underlying these somewhat complicated phenomena of solution.

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[*] I give such a deduction in the contemporary volume of the *Phil. Mag.*, May 1917.

[†] The vapour pressure of a solution is abnormal when it deviates from Raoult's law. In the same way osmotic pressure is abnormal when it deviates from the value given by the expression for an ideal solution, viz. $P - \frac{1}{2}\beta P^2 = \frac{RT}{V} \log e \frac{N + n}{N}$ (cf. Findlay's *Osmotic Pressure*, p. 31).

[‡] Cf. Bancroft, *Jour. Phys. Chem.*, 10, 322 (1906).

[§] I treat this problem more fully in a paper in the *Phil. Mag.*, September 1916, p. 295. A complete analysis of the problem of the effect of these physical factors on vapour pressure and osmotic pressure will appear in the coming number of the same magazine.

ADDENDUM TO ABOVE PAPER.

(*Added May* 10, 1917.)

The problem as to *why* the vapour pressure and osmotic pressure of a solution are related to its concentration and other properties can be approached by applying the kinetic theory of binary mixtures.*

As is well known, the vapour pressure of a pure liquid is determined partly by the thermal or bombardment pressure of the molecules inside the liquid, and partly by the attractive forces which the evaporating molecules have to overcome in travelling through the surface film. The bombardment pressure, which is equal and opposite in sign to the intrinsic pressure, is generally of the order of a few thousand atmospheres, whilst the work done is almost, but not quite, equal to the latent heat of vaporization of the liquid. If π is the heat or bombardment pressure, and A is the work done by the evaporating molecule against the inward pull at the surface, Dieterici has connected the vapour pressure p with π and A by the exponential equation $p = \pi e^{-A/RT}$. The most important assumption underlying this equation is that the vapour pressure above the liquid is proportional to the thermal pressure inside the liquid. The success which has attended the application of this equation seems to justify the assumption.†

The reason for the lowering of the vapour pressure on dissolving a non-volatile solute in a liquid is not so generally recognized. But it seems to be quite simple in the case of ideal solutions, when the solvent and the solute are neither polymerized nor dissociated nor combined with one another. When two substances are mixed together without appreciable change in total volume, each component of the mixture separates the molecules of the other component from one another. In consequence, the partial pressure of each component inside the solution is lowered; just as mixing two gases without total volume change reduces the partial pressure of each. Since the vapour pressure of the solvent above the liquid is proportional to the pressure of the solvent inside the liquid, it is clear that the vapour pressure of a solution is less than that of the pure solvent, because the thermal pressure of the solvent inside the solution is less than it is inside the pure solvent. Hence also the reason why the osmotic current is from the pure solvent to the solution: the flow takes place from the region where the thermal pressure of the solvent is the higher. Of course, the *total* pressure inside an ideal solution is more or less the same as the pressure inside the pure solvent. It is only the *partial* pressure of the solvent which is reduced by the process of solution. The relation between the partial and total pressures is given by Raoult's law. As in the vapour phase, the partial thermal pressure of each component inside the liquid is proportional to its molar fraction.‡

Then the vapour pressure of a solution is increased by the application of a hydrostatic pressure, because such a pressure forces the molecules of a liquid closer together, and so increases the internal pressures. As has just been indicated, an increase in the partial pressure of the solvent inside the solution necessitates an increase in the external vapour pressure, because of the aforementioned proportionality. Taking aqueous solutions as an example, if the thermal pressure inside pure water is 12,000 atmospheres say, the partial pressure of the water inside a molar cane-sugar solution would be about 11,800 atmospheres. Applying an external pressure of 22 atmospheres, i.e. the osmotic pressure, would raise it back to the 12,000 mark, so that osmotic diffusion between pure water and the solution under such a pressure would no longer take place.

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* I treat this problem fully in the *Phil. Mag.* for May 1917.

† See, for instance, McDougall, *Journ. Amer. Chem. Soc.*, xxxviii., p. 528 (1916)

‡ Cf. Tinker, *Phil. Mag.*, vol. xxxii., September 1916; ibid., May 1917.

Abnormalities in osmotic flow and the magnitude of the osmotic pressure seem to be caused by inequalities in the properties of the two surface films separating the membrane from the pure solvent and solution respectively. Consider, for instance, the case studied in the paper of a pure solvent and a solution separated by a vacuum. As is well known, the osmotic pressure of the solution is a function of the ratio of the vapour pressures of the pure solvent and solution respectively. Using dashed symbols for the solution, it is evident that for this ratio we can write $\frac{p}{p'}=\frac{\pi e^{-A/RT}}{\pi' e^{-A'/RT}}$. When the work performed (A′) by evaporating one molecule of the solvent from the solution is the same as that performed (A) by evaporating one molecule from the pure solvent, we have

$$\frac{p}{p'}=\frac{\pi}{\pi'}=\frac{N+n}{N}.$$

The vapour pressure of the solution is then given by Raoult's law, and the osmotic pressure of the solution is normal. If, on the other hand, the work performed by a molecule in getting through the surface film is not equal in the two cases, the ratio of the vapour pressures of the pure solvent and solution is a function also of the work difference at the two surface films. I have shown elsewhere * that this work difference, which is practically equal to difference in the latent heat of vaporization of the solvent and solution, is equal to the heat of dilution of the solution, and is also related to the difference in surface tensions, intrinsic pressures, etc., between the solvent and solution respectively. This is why the osmotic pressure of a non-ideal solution is a function of the latter factors as well as of the concentration of the solution.

In view of the comparatively large magnitude of the pressures inside liquids, the question naturally arises as to what pressure the solute would exert on an imaginary plane placed inside a dilute solution : is it equal to the pressure the solute would exert if it were in the gaseous state ? Apparently the answer to this question is that the bombardment pressure of the solute is *not* equal to the corresponding gas pressure. Perrin has indeed shown that the *average kinetic energy* of a molecule in the liquid state is the same as it is in the gaseous condition ; but this fact does not imply that the *average pressure* of a solute molecule must be same in the two states. The latter result would only follow provided the space available for molecular motion (i.e. the free space) were the same in dilute solutions as it is in dilute gaseous systems. As is well known, much of the available volume in dilute solutions is taken up by the solvent molecules ; with the result that the pressure which the solute could exert on the imaginary plane is considerably greater than the corresponding gas pressure.† If we regard it as legitimate to apply Raoult's law to the pressures inside aqueous solutions, taking the thermal pressure inside pure water as 12,000 atmospheres, the bombardment pressure which would be exerted by the sugar in a molar solution would be about 200–300 atmospheres—a figure ten times as great as the corresponding gas pressure. It is evidently a mistake to confuse the internal bombardment pressure of the solute with the osmotic pressure, which is an external mechanical pressure, and not a molecular pressure at all ; or with the pressure of a perfect gas, which is an entirely different physical quantity from either osmotic pressure or the real pressure of the solute. If this be the case, it may be asked : Why then is it that a membrane placed between a pure solvent and a solution is forced through the pure solvent with a pressure equal to that which would be exerted by a gasified solute? It is my personal opinion that this supposed gas analogy is not a real one; it overlooks the facts of the fundamental diffusion phenomena altogether. It is safest to consider osmotic phenomena in the first place without regard to molecular hypotheses at all, and to argue on lines somewhat as follows: Whatever the reason may be, it is in the nature of the osmotic process that the pure solvent should flow into the solution, and for the latter to increase in volume at the expense of the former. If the osmotic system is so constructed that the membrane is fixed whilst the solution is free to expand in a horizontal direction, no pressure whatsoever is exerted on the membrane; for it is an experimental fact that, in the absence of external pressure, osmotic diffusion can take place across the thinnest of membranes without these being ruptured or subjected to strain. As soon, however, as a mechanical pressure is placed on the surface of the solution, the side of the membrane in contact with the solution becomes subjected to a pressure also, viz. the pressure which is transmitted through the solution by virtue of the application of the external force. The same result is attained by allowing the solution to rise against gravity, when the solution side of the membrane becomes subject to a pressure equal to the weight of the column of liquid above it. The pressure on the membrane gradually increases with the height of the column; it is termed the osmotic pressure when the height is such that diffusion of the solvent can no longer take place. If, on the other hand, the solution is unable to move, it is clear that—by the principle of action and reaction—the membrane will tend to be displaced gradually through the pure solvent by the moisture which diffuses across it. Still, no appreciable force is exerted on the membrane until its motion is impeded and the solution thereby placed under compression. If the membrane is also fixed, such an amount of moisture will flow from the pure solvent into the solution as is sufficient to increase the compression on the latter to the point at which the mechanical pressure on the solution side of the membrane is sufficient to stop the inward flow.

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* Loc. cit.; the paper just mentioned.

† Cf. Nernst, *Theor. Chem.* ; English trans. of 6th German edition, p. 246.

It is therefore evident that the *modus operandi* of the usual osmotic system differs fundamentally from that in systems where gaseous pressures proper are exerted continuously and independently of other external pressures. The solute itself no more exerts a pressure on the membrane, in the sense that it tends to set up external motion, than it would do on the walls of a vessel in which the solution might be placed. The membrane is only subjected to a strain when the solution is compressed; the pressure is then exerted by the solution as a whole, and not by the individual molecules of the latter, whether of solvent or solute.

The fundamental similarity between a dilute solution and a perfect gas is that both experience no change in internal energy when their volume is varied. It is this fact which causes the equation of state to be similar for each; and provided that the vapour of the solution obeys Raoult's law, the maximum work which can be obtained by allowing a dilute solution to expand and go through a Carnot cycle is perforce the same as the work which can be obtained by causing a perfect gas to go through the same cycle.*

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* Application of the second law of thermodynamics alone gives for gaseous work the relationship $\frac{pv}{T}$ = const., and for osmotic work $\frac{PV}{T}$ = const. To prove that the two constants are the same, so that $\frac{pv}{T} = \frac{PV}{T}$, it is necessary to assume further that the vapour of the solution obeys Raoult's law.

This equality of maximum work does not prove that the physical mechanism of the two processes is the same in every detail; it merely shows that the second law of thermodynamics has a wide scope; and that when the law is applied to systems which are different in physical construction, the work which can be obtained by carrying out the process of expansion is independent of the nature of the medium employed; provided, of course, that the latent heat of the process has a constant value, whether zero or otherwise. Under these circumstances no theory of the osmotic mechanism can claim to be conclusive because it gives the simple "gas law" as a limiting case for dilute solutions.* Mechanical theories of osmosis are of no scientific value unless they throw light on the many abnormalities met with in osmotic phenomena generally, and unless they are capable of such development as will enable a full insight to be gained into the problem of the conditions inside liquids.

Sir Oliver Lodge: We shall now have the pleasure of hearing from Mr. Bousfield views based on a large number of experiments which he has been conducting for years, with admirable perseverance, on subjects akin to the present; and I expect that he will direct our attention to the important agency of the *solvent*.

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* It is of course quite easy to get the "gas law" by several different theories; and as easily by the vapour pressure theory, for instance, as by any other.

OSMOTIC PRESSURE IN RELATION TO THE CONSTITUTION OF WATER AND THE HYDRATION OF THE SOLUTE.

Mr. W. R. Bousfield, K.C., F.R.S., then read his Paper entitled "Osmotic Pressure in relation to the Constitution of Water and the Hydration of the Solute."

For the study of osmotic phenomena the relation of osmotic pressure to vapour pressure is of fundamental importance, and may be regarded as accurately based on a secure foundation of theoretical reasoning. But when it is desired to correlate the phenomena with the molecular proportions of the solvent and solute we are driven back on empirical relations. The study of the conductivity of electrolytes reveals a retardation of ionic velocities with greater dilution, which is attributable to the progressive hydration of the ions and which gives us a clue to the actual numbers of water molecules combined with them. Other physical phenomena throw further light on the number of combined water molecules. The expressions which correlate the osmotic data with the progressive hydration of the solute can only be tested by their accord with these physical results from other sources.

In considering the ultimate nature of the molecular conditions upon which the osmotic phenomena depend, two very different mental pictures have been presented by physicists. The one shows osmotic pressure as an internal "expansive force" depending on the energy and activity of the solute. The other exhibits osmotic pressure as an external pressure reacting against the activity of the solvent. The "vapour pressure" theory of osmotic pressure appears to decide finally between these views.

The nature of the solvent (water) has received very little attention in relation to osmotic phenomena, but it will be found that a consideration of the peculiar constitution of water enables a more comprehensive view of the whole subject to be envisaged.

In the present communication an attempt is made to bring to a focus various considerations in relation to these matters which are scattered through several former papers. These papers may conveniently be here enumerated, and reference afterwards made to them by the numbers appended.

I. "The Electrical Conductivity and Other Properties of Sodium Hydroxide," etc., Bousfield and Lowry, *Phil. Trans.*, A, 204, 253, 1905.

II. "Ionic Size in Relation to the Physical Properties of Aqueous Solutions," Bousfield, *Phil. Trans.*, A, 206, 101, 1906.

III. "Liquid Water a Ternary Mixture," Bousfield and Lowry, *Trans. Farad. Soc.*, 6, 85, 1910.

IV. "Ionization and the Law of Mass Action," Part II, Bousfield, *Trans. Chem. Soc.*, 105, 600, 1914.

V. Ditto, Part III, *Trans. Chem. Soc.*, 105, 1809, 1914.

VI. "Note on Osmotic Pressure," Bousfield, *Proc. R.S.*, A, 90, 41, 1914.

VII. "The Osmotic Data in Relation to Progressive Hydration," Bousfield, *Proc. R.S.*, 90, 544, 1914.

Röntgen[*] and Sutherland[†] established the probability that water consisted mainly of "ice molecules" or trihydrol $(H_2O)_3$ and dihydrol $(H_2O)_2$. A study of the "molecular volume" of sodium hydroxide in solution (I, 282) showed that it was necessary also to postulate the existence in water of "steam molecules" or simple hydrol (H_2O). Later this view was elaborated and fortified in a paper (III) which was a contribution to a general discussion by the Faraday Society on "The Constitution of Water," and as the outcome of this discussion the view that water consists mainly of trihydrol, dihydrol, and hydrol has been widely accepted. The proportions of these constituents at different temperatures have not yet been securely established. For the present purpose it will be sufficient to regard dihydrol as being the main component, the remainder at low temperatures being trihydrol, with a very small proportion of hydrol. As the temperature is raised the proportion of trihydrol steadily diminishes and that of hydrol notably increases.

The introduction of sugar or other solute into water at once reduces the proportions of both the trihydrol and the hydrol molecules (I, 282, and III). In fact, with a highly concentrated solution, such as a saturated solution of lithium chloride or a strong solution of sulphuric acid, it is probable that the whole of the free water is in the state of dihydrol, except for a minute proportion of hydrol, corresponding to the excessively minute vapour pressure.

The vapour pressure of water or an aqueous solution is necessarily closely connected with the proportion of simple steam molecules existing at any given temperature and concentration. Hence, as we should expect, the introduction of any solute into water, by lowering the proportions of both ice and steam molecules, depresses both the freezing-point and vapour pressure of the solution. Here, then, we are brought to the threshold of the osmotic phenomena.

The application of thermodynamics to elucidate the conditions of osmotic equilibrium has given us two different conceptions which have been applied to interpret the facts. The first, which is due to van't Hoff, and is a rough approximation only, tells us that the osmotic pressure of a solution is the same as if the solute existed alone in the form of a gas in the space occupied by the solution. It is really a purely formal statement of an algebraical equation, and if used as a basis for a mental picture of the molecular conditions involved will lead us astray. The second conception, due to Callendar, Porter, and others, that osmotic equilibrium depends on equality of vapour pressures produced by the compression of the solution, appears to have a high order of accuracy and leads to a totally different picture. These physicists have demonstrated that—

1. When a solution is in osmotic equilibrium with the pure solvent through a semi-permeable membrane the vapour pressures of the solution and the solvent are the same.

2. To produce this equilibrium the solution must be under sufficient liquid pressure to raise its vapour pressure to the required equality.

3. The general relation between liquid pressure and vapour pressure is—

$$U dP = v dp.$$

In this expression U is the specific volume of the solvent at pressure P and v the specific volume of the vapour at pressure p. Thus the law may be expressed by saying that the rate of change of vapour pressure with liquid pressure is proportional to the ratio of the specific volume of the solvent to that of the solute. But it should be noted that U is not the specific volume of pure water, but the specific volume of the water *as it exists in the solution.* The solute combines with some of the water, and in so doing eliminates some of the ice and steam molecules from the free water, so that the constitution of the free water is changed by the solute. U is the mean specific volume of the water of the solution thus changed. Put into other language, we may say that U is the change of volume which takes place on the addition of a gram of water to an infinite quantity of the solution.* It is important, however, to remember that U is simply the mean specific volume of the water in the solution.

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[*] *Wied. Ann.*, 45, 91, 1891.

[†] *Phil. Mag.* (5), 50, 460, 1900.

With the aid of these propositions accurate definitions can be formulated and the fundamental relation between osmotic pressure and vapour pressure deduced.

Definition I.—The vapour pressure of a liquid is the pressure of the vapour with which it is in equilibrium under pressure of its own vapour only.

Definition II.—The internal vapour pressure at a point within a solution is the pressure which would exist within a small sphere placed at the point permeable only to the vapour of the solvent.

Definition III.—The osmotic pressure of a solution of given uniform concentration at a given temperature is the liquid pressure under which the internal vapour pressure of such solution is equal to the vapour pressure of the pure solvent.

Osmotic pressure is thus defined as a physical quantity dependent only on the concentration and temperature of the solution. It is *not* a thing which can vary from point to point of a solution of uniform temperature and concentration in accordance with the variation of the liquid pressure. Such a conception of osmotic pressure can only lead to confusion.

This confusion has arisen from thinking of osmotic pressure in terms of a column of solution with a free vapour surface at the top, supported at the bottom by a semi-permeable membrane with the pure solvent below it. It leads to an expression for the osmotic pressure at the bottom of a column in terms of vapour pressure at the top of the column and to ideas as to the "variation of osmotic pressure with hydrostatic pressure" which are inimical to clear thinking.

The relation of osmotic pressure to vapour pressure is simplified if we consider only a small elementary portion of a solution not in contact with a semi-permeable partition. The idea of a semi-permeable partition gives us the definition of internal vapour pressure. Then we need only take a small mass of solution of given temperature and concentration subjected to such a liquid pressure as to make its internal vapour pressure equal to the vapour pressure of the pure solvent. Such liquid pressure is the osmotic pressure of the solution. The fundamental relation between osmotic pressure and vapour pressure will be deduced in this way.

A mental picture of the way in which the compression of the solution affects the internal vapour pressure is useful. It can be shown that we may regard the vapour of the solution as existing in the molecular interspaces and behaving there approximately as a perfect gas. Upon this view the compression of the solution reduces the molecular interspaces and proportionately increases the vapour pressure. This is not the only factor in the case of a complex liquid such as water, but it indicates that the compressibility of water plays a primary rôle in the phenomena, instead of being, as treated by some writers, a secondary incident which is merely a matter for a correction. Thus we find in one of the latest papers[*]:—

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* Bousfield, *Trans. Chem. Soc.*, 107, 1409, 1905.

"At the pressures measured in this work the compressibility of the solution is no doubt an important factor. However, no data were available, so this factor was neglected."

According to the present view, the compression of the solution, which is the means by which the vapour pressure is raised to the required equality with that of water, plays the leading rôle.

The compressibility of water depends mainly on two factors. The dense dihydrol may be regarded for our present purpose as approximately incompressible. But both ice and steam molecules are bulky molecules (I, 283), which yield to pressure in different ways. A proportion of the ice molecules is destroyed by pressure, and since the volume must be reduced by pressure the reaction is probably rather $2(H_2O)_3 = 3(H_2O)_2$ than $(H_2O)_3 = (H_2O)_2 + H_2O$. Hence compression, so far as it results in destroying ice molecules, can do little towards raising the vapour pressure.

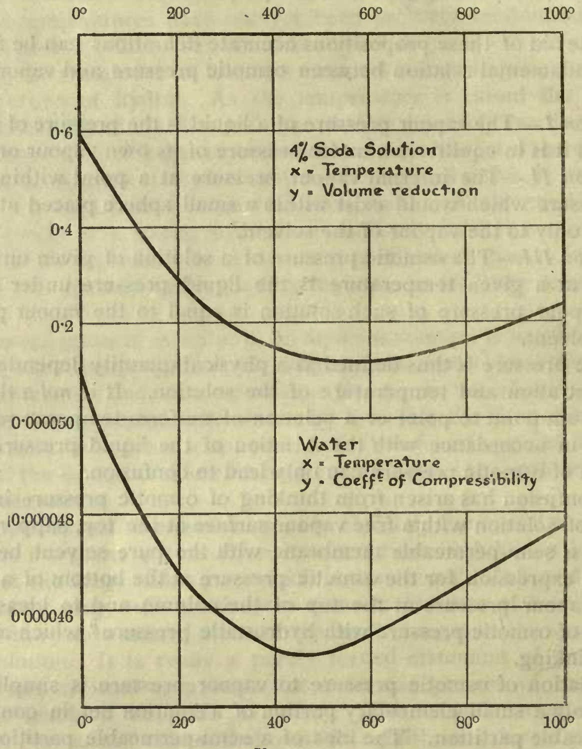

FIG. 1.

But the steam molecules must be regarded as bulky and compressible, not because of their peculiar structure, but because of their superior activity, which results in their occupying more space than that to which their size would entitle them. The actual size of the steam molecule is probably less than a third of that of the ice molecule. But the curves given in a former paper (I, 315) tend to show that the simple steam molecule may occupy a larger space than the ice molecule, which is thrice as heavy. The size of the steam molecule as deduced from density measurements is, of course, the size of the free space which it occupies owing to its vibratory activity.

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[*] Frazer and Myrick, *Journ. Am. Chem. Soc.*, 38, 1919, 1916.

When 4 grams of sodium hydroxide are dissolved in 96 grams of water at 0° C., the total volume is 0·6 c.c. less than that of the original water. The upper curve in Fig. 1 shows the reduction of volume which takes place at temperatures from 0° to 100°. The lower curve in the figure exhibits the change in the compressibility coefficient of water over the same range of temperature for compression from 1 to 100 atmospheres. Both curves tell the same tale. The rise of the curves towards the left tells of the greater destruction of ice molecules in the region near 0° C., where the ice molecules are more numerous, the destruction being in the one case due to the action of the solute and in the other case to pressure. The rise on the right in the region approaching 100° tells in both cases of the greater abundance of steam molecules as the higher temperature is approached, which results in the one case in the greater destruction of steam molecules by the influence of the solute, and results in the other case in the greater compressibility of the water owing to the existence of so much more compressible interspace occupied by the steam molecules. The curves both show a less rise on the right side than on the left, which might at first sight lead us to suppose that steam molecules were less compressible than ice molecules. But it must be remembered that the ice molecules near 0° are many times more numerous than the steam molecules near 100°, and we may fairly conclude from the curves that the space occupied by a steam molecule is a good deal larger than that occupied by the thrice heavier ice molecule.

These considerations lead to the conclusion that compression, so far as it merely results in the destruction of ice molecules, is comparatively ineffective in raising the vapour pressure of water, whilst compression which reduces the comparatively large molecular interspaces occupied by steam molecules has a higher efficiency in increasing vapour pressure. The resulting vapour pressure for isothermal compression is probably approximately proportional to the number of steam molecules per gram of water divided by the total space which they occupy.

These conclusions are in conformity with the results of Morse and his co-workers,* who found by a series of careful experiments that the osmotic pressure of a decinormal sucrose solution is actually *greater* at 0° C. than at 5° C. The result is easily explained by the consideration that owing to the presence of more ice molecules at 0° C. the efficiency of liquid pressure in increasing vapour pressure is less at 0° C. than at 5° C. Consequently the pressure required for bringing up the vapour pressure to the required point is greater—in other words, the osmotic pressure must be greater. No other explanation of the abnormality is forthcoming. The abnormality gradually disappears with increasing concentration, and has practically disappeared before half-normal concentration is reached. Higher temperature, like higher concentration, by destroying a proportion of the ice molecules, reduces the disturbance to small proportions, but it will be seen that even at 20° C. their effect is apparent in the more dilute solutions.

For the purpose of developing the relation between liquid pressure and vapour pressure from the equation—

$$\mathrm{U}d\mathrm{P} = v\,dp,$$

we shall find that we can get a close approximation by taking v as following the gas law. But the functional expression of U (for which experimental data are very deficient) is necessarily of a complex character. The specific volume of the water in the solution depends on the proportions of trihydrol and hydrol, which themselves depend not only on temperature but on concentration. Fortunately, when we get away from the freezing-point, even as far as 20° C., the proportion of ice molecules is sensibly reduced by temperature, and when we are dealing with solutions as strong as half-normal there is a still more notable destruction of the ice molecules. Owing to this it will be found that a very simple hypothesis as to the variation of U will give excellent results for solutions which are not too dilute or, if dilute, are not too near the freezing-point.

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* *Am. Chem. J.*, 45, 502, 1911.

The study of the density of a number of aqueous solutions shows that the specific volume of the water in the solution is within two or three parts per thousand the same as the specific volume of pure water. For the isothermal variation of U with liquid pressure we shall therefore assume a simple linear law similar to that which expresses approximately the isothermal variation of the specific volume of water. Let—

$p_0 =$ vapour pressure of a solution under pressure of its own vapour only.
$p_w =$ vapour pressure of water under pressure of its own vapour only.
$\delta p = p_w - p_0$, the vapour pressure lowering of the solution.
$P =$ liquid pressure of the solution.
$U_0 =$ value of U when $P = p_0$.

Let us assume $U = U_0[1 - \beta(P - p_0)]$.

Since the magnitude of β is of the order 0·00005, we for the purpose of integration take—

$$U = U_0[1 + \beta(P - p_0)]^{-1}.$$

For the relation between the pressure and specific volume of aqueous vapour let us take the gas equation—

$$p\,\frac{ve}{1{,}000} = RT \quad \text{or} \quad v = R'T/p,$$

where R is the gas constant 0·0821 and $R' = 1{,}000R/e = 4·557$, e being the molecular weight of steam, taken as 18·016.

On substitution of these values for U and v in the equation—

$$U\,dP = v\,dp$$

and integrating we obtain—

$$\frac{U_0}{\beta}\log[1 + \beta(P - p_0)] = R'T\log(p/p_0)$$

as the general relation between liquid pressure and vapour pressure at constant temperature. The integration constant is obtained from the consideration that when $P = p_0$ we have also $p = p_0$. We thus obtain P in terms of p, but it is important to note that P never represents osmotic pressure except when $p = p_w$. Putting $p = p_w$ we get for the osmotic pressure—

$$\log[1 + \beta\overline{P - p_0}] = \frac{\beta R'T}{U_0}\log(p_w/p_0),$$

which, by putting $\delta p = p_w - p_0$, expanding the logarithms, neglecting small quantities of the second order, and neglecting p_0 in comparison with P on the left-hand side, becomes—

$$\frac{P}{R'T} = \frac{1}{U_0}\cdot\frac{\delta p}{p_w}.$$

P now stands for osmotic pressure. This is the fundamental relation between osmotic pressure and vapour pressure which has already been obtained by Callendar and Porter, but the present approximate proof is given to show that the relation follows immediately from the strict definition, with simple assumptions as to the functional forms of U and v which are undoubtedly true over a limited range of pressure and temperature.

It should be noted that in the above proof there is no question of vapour pressure over a free surface, but only of internal vapour pressure as above defined. We deal only with the internal vapour pressure of a small mass of the solution which is subjected to external liquid pressure. We have assumed that the *internal vapour pressure* obeys the gas law, and the fact that we are led to the well-known result, coupled with the practical application of this result which follows later, indicates that our assumption is justified. In other words, it shows that we may regard the vapour (or steam molecules) in the molecular interspaces of the solution as behaving approximately as a perfect gas. We can arrive at this result in another way, which at the same time gives us an idea of the actual volume per litre of the molecular interspace in which the steam molecules exercise their activity.

Let a litre of solution be subjected to a pressure P. The change of volume produced by such pressure is approximately—

$$\delta V = \beta P.$$

Let us neglect the compression of dihydrol and that produced by destruction of ice molecules, attributing the whole compression to the reduction of the molecular interspaces in which the steam molecules are active. Let V_0 be the initial molecular interspace filled by vapour in a litre of solution under no pressure except that of its own vapour. Let the solution be now compressed to a pressure equal to its osmotic pressure P. The interspace volume is reduced to $V_0 - \delta V$ and its internal vapour pressure is increased from $p_w - \delta p$ to p_w. Then if the interspace vapour behaves as a perfect gas we have—

$$p_w(V_0 - \delta V) = (p_w - \delta p)V_0 \quad \text{or} \quad V_0\delta p = p_w\delta V,$$

and since $\delta V = \beta P$ we have—

$$P = \frac{V_0}{\beta} \cdot \frac{\delta p}{p}.$$

If we compare this with the known thermodynamical result—

$$P = \frac{R'T}{U_0} \cdot \frac{\delta p}{p}$$

the two are in agreement if

$$V_0 = \beta R'T/U_0,$$

or taking $\beta = 0{\cdot}00005$ and $U_0 = 1$ the required molecular interspace is about 66 c.c. per litre at 15° C.

These considerations justify us in visualizing the phenomena of osmotic pressure as depending on the activity of the steam molecules in the molecular interspaces instead of the activity of the molecules of the solute giving rise to an "expansive force." It is not the expansive force of the solute but of the solvent which gives rise to the phenomena. It is the vapour of the solvent instead of the solute which behaves as an enclosed gas.

Passing now to the consideration of the osmotic phenomena in relation to the hydration of the solute, it will be found that the following general relations conform to a variety of experimental data, both for electrolytes and sucrose within the limits of experimental accuracy, except in the region of dilute solutions at low temperatures. These relations may be concisely expressed thus—

$$\frac{P}{R'T} = \frac{\delta p}{p} = \frac{\Delta}{F'} = \frac{i}{h-n}.$$

For simplicity of reference they may be denoted by—

$$A = B = C = D$$

In the above expressions—

$$R' = R\,\frac{1{,}000}{e} \qquad F' = F\,\frac{1{,}000}{e},$$

where $e = 18{\cdot}016$, the molecular weight of steam, and R and F are the ordinary gas equation and freezing-point constants.

Taking—

$$R = 0{\cdot}0821 \quad \text{and} \quad F = 1{\cdot}867$$

we have—

$$R' = 4{\cdot}557 \quad \text{and} \quad F' = 103{\cdot}6.$$

Further—

$P =$ osmotic pressure.
$p =$ vapour pressure of water.
$\delta p =$ vapour-pressure lowering of solution.
$\Delta =$ freezing-point lowering.
$i = 1 + a$ where $a =$ ionization of solution.
$h =$ molecules of water (reckoned as H_2O) per molecule of solute.
$n =$ molecules of combined water per molecule of solute.
$h - n =$ molecules of free water per molecule of solute.

The above expression embodies six relations. The empirical proof rests upon examples given in the former papers which may be here recapitulated.

As regards the member $A = B$, this is the fundamental result before given, simplified by taking $U_0 = 1$. The result involving U_0 is only reached by a series of approximations, and the application of the expression in practice indicates that the simple relation $A = B$ has a high order of accuracy without including U_0. Moreover, the difference arising from putting $U_0 = 1$ is generally less than 2 per 1,000, whilst the order of accuracy of vapour pressure measurements is not greater than 1 in 100.

As regards the member $C = D$, this was originally obtained by a consideration of the volume of water combined with the ions of potassium chloride, as derived from the retardation of the water-logged ions which is indicated by conductivity measurements, in conjunction with Jahn's experimental values for the freezing-point depression. It was shown (II, 148) that if the molecular depression of the freezing-point were reckoned upon the *free water*, instead of the *total water*, a constant value was obtained; that is to say, it was shown that—

$$\frac{\Delta}{Ni} \cdot \frac{w}{1{,}000} = F = 1{\cdot}867,$$

where w is the free water in 1,000 grams of water and N is the molecular concentration of the solute per 1,000 grams of water. Since—

$$N = \frac{1{,}000}{he} \quad \frac{w}{1{,}000} = \frac{h-n}{h} \text{ and } F' = F\,\frac{1{,}000}{e},$$

we can put the expression into the form—

$$\frac{\Delta}{F'} = \frac{i}{h - n},$$

which is the relation C = D above given.

This relation has since been found to give accurate results in every case in which it has been tested. A difficulty is that the value of F derived from freezing-point measurements of different observers is found to vary. The value 1·867 was deduced from Jahn's freezing-point determinations in the case given above. Bedford's figures * give values from 1·86 to 1·867. Morse and Frazer's figures † for sugar solutions give the value 1·855.

The relation A = D is founded primarily on the measurements of the osmotic pressures of sucrose solutions at 20° C. by Morse and his co-workers,‡ in conjunction with Morse and Frazer's freezing-point determinations. There is a slight loss of accuracy in considering osmotic pressures at 20° in conjunction with freezing-point values, since there is probably a slight variation in the value of n as between 20° C. and 0° C., but the marked abnormality of osmotic pressure measurements at 0° C. renders them unsuitable for the foundation of the general law.

Morse and Frazer found that their freezing-point values for sucrose solutions could be simply expressed in terms of the densities by the relation—

$$\Delta/N = F\rho.$$

To derive the values of n from these values of Δ we may use the relation C = D, which is (since i is unity in the case of sugar)—

$$\frac{\Delta}{F'} = \frac{1}{(h - n)},$$

which gives by substitution $n = h\left(1 - \frac{1}{\rho}\right)$.

The values of n given by this expression are smoother than those derived from individual values and probably more accurate. They are set out in Table I. Let us now calculate the osmotic pressures of sucrose solutions at 20° by means of the relation A = D, that is to say—

$$P = \frac{R'T}{h - n},$$

from the values of n calculated from the freezing-points. It should be observed that we have no constant by which the figures can be adjusted, since we take the gas constant as accurately R = 0·0821, giving R′ = 4·557

The calculated values of P are set out in Table I, together with the observed values and the differences, from which it will be seen that, except for the three most dilute solutions, the differences are well within the limits of experimental error, which may arise both in the values of n and in those of P. Further, it may be remarked that the differences in the three most dilute solutions are less than the experimental differences between Berkeley and Hartley § and Morse and his co-workers. Moreover, it may be pointed out that in the earlier determinations of Morse and Frazer the mean of eleven

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* *Proc. R.S.*, A, 83, 454, 1910.
† *Am. Chem. Journ.*, 34, 1, 1905.
‡ *Ibid.*, 48, 29, 1912.
§ *Proc. R.S.*, A, 92, 483, 1916.

experiments gave the osmotic pressure at 18° for N = 0·1 as 2·41, which is practically identical with the present calculated value. But it seems probable that the rise of the first three experimental values above the calculated values is a genuine phenomenon, attributable to the fact that at 20° the ice molecules are still so numerous in dilute solution as to require an abnormally high liquid pressure to raise the vapour pressure of the solution

TABLE I.

Sucrose Solutions.

N.	*h.*	*n.*	P Observed.	P Calculated.	Difference.
0·1	555·06	6·11	2·59	2·43	− ·16
·2	277·53	6·36	5·06	4·92	− ·14
·3	185·02	6·30	7·61	7·47	− ·14
·4	138·76	6·18	10·14	10·07	− ·07
·5	111·01	6·03	12·75	12·72	− ·03
·6	92·51	5·88	15·39	15·41	+ ·02
·7	79·29	5·73	18·13	18·15	+ ·02
·8	69·38	5·59	20·91	20·93	+ ·02
·9	61·67	5·45	23·72	23·75	+ ·03
1·0	55·51	5·31	26·64	26·60	− ·04

to the required equality with that of water. Also, it should be observed that the true values of *n* at 20° are possibly slightly smaller than those set out, which are derived from freezing-point measurements.

It is true that the values of *n* given by Philip for 15° C.,* viz.

$$\begin{array}{llll} h = 95 & 44 & 38 \\ n = 6·7 & 5·9 & 5·4 \end{array}$$

are slightly higher, but those derived from freezing-points are to be preferred. Slightly smaller values for *n* would make the calculated values for the five most dilute solutions practically identical with the observed values.

Berkeley and Hartley † have determined the osmotic pressures of more concentrated sucrose solutions at 0°. Their figures are given in Table II, together

TABLE II.

Sucrose Solutions at 0° *C.*

h.	P.	*h* − *n.*	*n.*
55·95	24·55	50·90	5·05
23·37	67·74	18·45	4·92
17·00	100·13	12·48	4·52
13·46	134·84	9·27	4·19

with the values of *n* calculated therefrom by means of the relation A = D. These values of *n* are in good accord with the values of *n* calculated in the same way from Morse's determinations at 20° C. (V, 604), and carry on the series into the region of more concentrated solutions, where it appears that the disturbing influence of the ice molecules is no longer felt even at 0° C. At dilutions greater than half-normal Morse's figures give too high values for n, whilst those of Berkeley and Hartley give too low values. It ought to be possible to get a closer agreement in the experimental values in these more dilute solutions. The agreement at normal dilution is excellent.

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* *Trans. Chem. Soc.*, 91, 711, 1907.

† *Proc. R.S.* A, 92, 483, 1916.

It is worth while noticing what would be the effect of including U_0 in the expression. In the case of sucrose, the densities at 20° have been studied in a former paper,* and the accurate value of U_0 up to beyond normal concentration is given by the empirical expression—

$$U_0 = w - \frac{6{\cdot}2\ E}{(E + H)^2},$$

where w is the specific volume of water, E is the molecular weight of sugar (taken as 342·2), and H is the weight of water in which E grams of sugar are dissolved. This formula gives the values of U_0 at 20° as ranging from 0·998 at decinormal dilution to 0·997 at normal dilution. If the calculated values for P in Table I are divided by the corresponding values of U_0, the calculated results for the more dilute solutions will be hardly altered, whilst for the more concentrated solutions the calculated values become a little too large instead of too small. With the available accuracy of experimental determinations of n and P the simple expression $A = D$ is thus found to hold within the limits of experimental error in solutions which are not too dilute and too near the freezing-point.

It has now been shown that within the limits of experimental error the relations $C = D$ and $A = D$ hold in the cases studied, and as we have from thermodynamics the relation $A = B$, we get the whole set—

$$A = B = C = D.$$

Striking confirmation of these relations and a direct test of the relation $B = D$ has been obtained (V, 1818) by the study of the chlorides of potassium, sodium, and lithium, for which good freezing-point, vapour-pressure, and conductivity data are available. In the case of sugar, ionization could be neglected. In the case of these strong electrolytes it is a very important factor, and the deduction of an accurate ionization law was necessary. It was shown that for these substances the ionization law

$$\frac{a^2}{1 - a} = K(h - n)^{\frac{1}{2}}$$

satisfies all the conditions of the problem. We are thus enabled to obtain separate series of values of n from the freezing-point data and the vapour-pressure data, which are found to be in accord with one another and also with the values of n which result from the consideration of the retardation of ionic velocities by the water of hydration which is carried by the ions.

By combining the osmotic relations with the ionization relation we get the expressions

$$\frac{a^4}{(1 - a)^2(1 + a)} = \frac{K^2}{\Delta/F'} = \frac{K^2}{\delta p/p},$$

from which the ionization can be reckoned. The values of n can then be obtained from the osmotic relations

$$h - n = \frac{1 + a}{\Delta/F'} = \frac{1 + a}{\delta p/p}.$$

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* Bousfield, *Trans. Chem. Soc.*, 107, 1423, 1915.

The concordance of the two sets of values of *n* arising from the independent values for Δ and $\delta p/p$ furnishes the final confirmation of the truth of the relation B = C = D. For the complete proof reference must be made to the original paper (V). But the results for lithium chloride may be set out, and when plotted on a diagram show the concord in a striking manner.

TABLE III.

Values of n from Freezing-point Data for LiCl.

h.	Δ.	$\text{Log}\,\frac{\Delta}{F'}$.	$\text{Log}\,\frac{K^2}{\Delta/F'}$.	*a*.	*h* − *n*.	*n* Observed.	*n* Calculated.
28·95	8·57	$\bar{2}$·91761	$\bar{1}$·67279	0·5934	19·26	9·69	8·5
34·95	6·587	$\bar{2}$·80332	$\bar{1}$·77648	0·6150	25·40	9·55	9·4
36·54	6·218	$\bar{2}$·77830	$\bar{1}$·79930	0·6198	26·99	9·55	9·6
47·24	4·625	$\bar{2}$·64972	$\bar{1}$·91928	0·6445	36·84	10·40	10·5
76·28	2·713	$\bar{2}$·41814	0·14086	0·6893	64·50	11·78	12·2
104·51	1·941	$\bar{2}$·27277	0·28183	0·7166	91·60	12·91	13·2
164·12	1·217	$\bar{2}$·07004	0·48096	0·7536	149·24	14·88	14·6

TABLE IV.

Values of n from Vapour-pressure Data at 18° C. for LiCl.

h.	$\delta p/p$.	$\frac{K^2}{\delta p/p}$.	$\text{Log}\,\frac{K^2}{\delta p/p}$.	*a*.	*h* − *n*.	*n* Observed.	*n* Calculated.
7·278	0·326	0·0862	$\bar{2}$·93551	0·4432	4·43	2·85	2·8
10·40	0·229	0·1227	$\bar{1}$·08884	0·4733	6·43	3·97	4·0
16·25	0·140	0·2007	$\bar{1}$·30255	0·5165	10·83	5·42	5·6
29·19	0·073	0·3849	$\bar{1}$·58535	0·5752	21·58	7·61	7·8

The two series overlap at about $h = 29$, and show at this point that the value of *n* is greater at the lower temperature than at 18°. But the value of *a* is also greater, which is in conformity with the requirements of the theory that ionization depends on water combination.* In fact, the *two* series of values of *n* when plotted on the values of *a*, as shown in Fig. 2, give a nearly straight-line law, which may be expressed as

$$n = 38a - 14.$$

The values of *n* calculated from this expression are set out in Tables III and IV, and are in good agreement with the "observed" values derived from the experimental data by means of the relations B = C = D.

At infinite dilution, when $a = 1$ the expression gives $n = 24$, which is in good accord with the value derived from conductivity measurements.† The values for a saturated solution of lithium chloride come out as

$$h = 3 \qquad n = 1{\cdot}4 \qquad a = 0{\cdot}4$$

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* See Bousfield and Lowry, *Trans. Farad. Soc.*, 3, p. 123, 1907.

† Bousfield, *Proc. R.S.*, A, 88, 168, 1912.

almost exactly, which give an equation for the reaction of lithium chloride and water which is in accord with the law of mass action (V, 1823). The confirmation of the relation $B = C = D$ appears to be as complete as it is possible to make it.

No reliable osmotic pressure determinations for strong electrolytes are yet available. But the above relations enable us to calculate the osmotic pressure with an accuracy probably greater than can be realized experimentally. The osmotic pressures for the more concentrated lithium chloride solutions calculated from the above data are as follows :—

$h =$	7·278	10·40	16·25	29·19
$P =$	432	304	186	97 atmos.

For a saturated solution of lithium chloride at 18° C. we have

$$h = 3 \qquad n = 1{\cdot}4 \qquad a = 0{\cdot}4$$

so that the osmotic pressure would be over a thousand atmospheres.

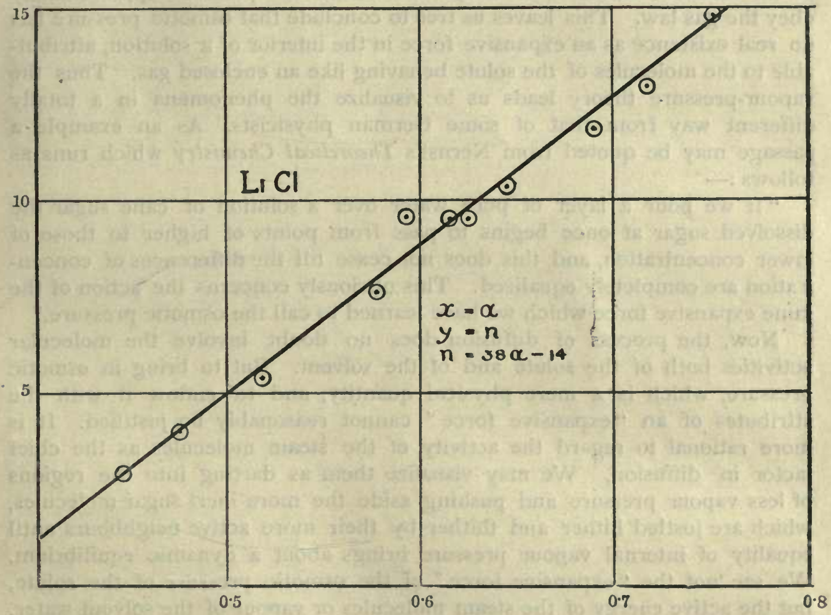

FIG. 2.

To recapitulate : it has been shown that the strict definition of osmotic pressure given above leads through the relation $U\,dP = v\,dp$ to the fundamental relation—

$$\frac{P}{RT} = \frac{1}{U_0} \cdot \frac{dp}{p}.$$

The osmotic pressure of a solution thus appears as a definite physical quantity like density, viscosity, etc., depending only on temperature and concentration.

Further, it appears that there is no sensible loss of accuracy, within the limits of experimental error, by putting $U_0 = 1$, and that, except in the region where the large proportion of ice molecules produces abnormal results, the group of relations

$$\frac{P}{R'T} = \frac{dp}{p} = \frac{\Delta}{F'} = \frac{i}{h-n}$$

correlates the osmotic data with the hydration of the solute with great accuracy, giving values of n which are consistent *inter se*, and also with values derived from other physical data. Moreover, these relations hold with the greatest accuracy in the most concentrated solutions, where the effect of the solute upon the solvent is to simplify its constitution (I, 283) and produce more "ideal" conditions. But it must be remembered that an "ideal" solution from the point of view of osmotic pressure is one in which the solute acts upon the solvent so as to produce a progressive lowering of freezing-point and vapour-pressure values, accompanied by the progressive hydration of the solute itself according to the law of mass action (V, 1823).

It has also been shown that the osmotic phenomena may be interpreted as resulting from the activity of steam molecules in the molecular interspaces of the solution, which when subjected to external pressure approximately obey the gas law. This leaves us free to conclude that osmotic pressure has no real existence as an expansive force in the interior of a solution, attributable to the molecules of the solute behaving like an enclosed gas. Thus the vapour-pressure theory leads us to visualize the phenomena in a totally different way from that of some German physicists. As an example a passage may be quoted from Nernst's *Theoretical Chemistry* which runs as follows:—

"If we pour a layer of pure water over a solution of cane sugar the dissolved sugar at once begins to pass from points of higher to those of lower concentration, and this does not cease till the differences of concentration are completely equalized. This obviously concerns the action of the same expansive force which we have learned to call the osmotic pressure."

Now, the process of diffusion does no doubt involve the molecular activities both of the solute and of the solvent. But to bring in osmotic pressure, which is a mere physical quantity, and to endow it with the attributes of an "expansive force" cannot reasonably be justified. It is more rational to regard the activity of the steam molecules as the chief factor in diffusion. We may visualize them as darting into the regions of less vapour pressure and pushing aside the more inert sugar molecules, which are jostled hither and thither by their more active neighbours until equality of internal vapour pressure brings about a dynamic equilibrium. We see not the "expansive force" of the osmotic pressure of the solute, but the active energy of the steam molecules or vapour of the solvent water.

If we consider the case of a solution enclosed in an inextensible semi-permeable envelope immersed in water, it is not an internal force but an external force which produces the internal pressure required for equilibrium. The water vapour in the external water is projected through the envelope in sufficient amount to raise the internal vapour pressure to equilibrium pressure. This is exactly analogous to Ramsay's classical experiment with a palladium diaphragm permeable to hydrogen but not to nitrogen. If a closed envelope of palladium be filled with nitrogen and immersed in an atmosphere of hydrogen, the hydrogen will pass into the envelope until the pressures of hydrogen within and without tend to equality, independently of the pressure of the nitrogen. The nitrogen plays an inert part which is similar, according to the vapour-pressure theory, to that of the solute in the solution. Both take up a certain amount of space, but the determining factor is the equality of the vapour pressure of the constituent which passes through the semi-permeable membrane on the two sides thereof. The rôle of the solute in the case of aqueous solutions is to *decrease* the activity of the solution by destroying some of the steam molecules on which its vapour pressure depends and not to *increase* its activity. In other words, osmotic pressure as a "force" is non-existent.

ST. SWITHIN'S, HENDON, N.W.

DISCUSSION.

Mr. W. R. Bousfield : I think it will be best if I devote a few minutes to a criticism of Professor Porter's paper, and point out what occur to me to be some of the flaws in the reasoning he has put forward ; because we have our different views, and from my point of view I cannot help thinking that the theory of osmosis and osmotic pressure which endows the solute with activity and leaves out of account, comparatively speaking, the activity of the solvent, is quite the wrong way of looking at it. Suppose this glass holding water for drinking is instead half filled with sugar solution : I should like to ask Professor Porter whether there would be any osmotic pressure in that exercised anywhere. The theory that the solute is endowed with the activity of a gas demands that the question should be satisfactorily answered. Again, Dr. Porter says that no theory of osmotic pressure is any good unless the theory takes account of the Brownian movement, the dynamics of the solute. But suppose I have a mass of liquid mercury in a vertical glass tube with a flat bottom and a vacuum above : my theory of the pressure on the bottom of the cylinder would be that it was due to gravity and was equal to the weight of the mercury. Professor Porter's argument would suggest that this theory is no good because it takes no account of the Brownian movements in the mercury.

Now let me come to the long trough described by Professor Porter, with a diaphragm in the centre, one end being filled with a strong sugar solution and the other with water. Take out the diaphragm, and what happens ? Dr. Porter says : "In order to prevent diffusion a force from right to left must be introduced, acting only upon the sugar." Surely that is a misconception. There is a thing that one used to call the equation of continuity. The volume of sugar which passes the central section in one direction is exactly equal to the volume of water coming in the other direction, so that instead of putting demons to stop the sugar coming one way you will equally well stop diffusion by putting demons to stop the water coming the other way, because the oppositely moving volumes of the water and the sugar solution must be precisely equal. I suggest that it is in the main the activity of the vapour particles in the water which causes diffusion. If a certain number of vapour particles push in one direction into the sugar solution, that means an equivalent volume of sugar particles are pushed in the reverse direction. Professor Porter says that the pressure of sugar arises from its thermal motion and that Perrin has given evidence that this is the same as for a gas. One would like to cross-examine that evidence. Consider the free surface of a solution under the thermal bombardment of those sugar particles which are supposed to be so active and to give this enormous pressure. Compare this bombardment with that of the water particles which I say are the real active things and which do the business. What happens at the free surface ? These very active sugar particles cannot get through the surface at all. It is the vapour particles that get through the surface. If there is a bubble of water, it may carry up some sugar, but apart from anything of that sort, suppose you put my solution in a bell jar, evacuated : in an instant of time the whole thing is filled with water vapour ; the activity of the vapour fills the whole space ; the activity of the sugar does not enable an appreciable molecule to break through the surface. It seems to me that it is absurd, when these are the relative activities of the things, to endow the solute with all that activity when as a matter of fact you have got an all-sufficient cause in the activity of the vapour itself. Just a word further. How does the suggested gas relation $P(v - b) = RT$ get into the osmotic equation at all ? It comes from the assumption that one makes that the *internal vapour* obeys the gas law in deducing the relation of osmotic pressure to vapour pressure from the formula of Professor Callender, $UdP = vdp$. That is the whole relation between liquid pressure and vapour pressure, and in developing that either in Professor Porter's way or Lord Berkeley's way or Professor Callender's way, in either case as an approximation you assume that water vapour obeys the gas law, and so get RT into the result. Not merely mathematically, but also practically, it turns out to be true that the occluded vapour, the vapour which exists in the free state inside the solution, obeys the gas law when it is compressed in the solution. In the deduction of the relation between vapour pressure and osmotic pressure, that is where the gas law comes in, and it simply comes to this, that the whole of the osmotic relations can be worked out from the simple principle that the vapour within the solution obeys the gas law. You get it into the equation in that way. It is a mere matter of algebraical expression, and it does not lead to any supposition that the solute itself should obey the gas law. That is how it comes into the equation, and when it is there it accounts fully for the whole theory of the relation between osmotic pressure and vapour pressure. When you have the fact that the internal vapour pressure obeys the gas law, and that this behaviour gives you a theory which fits the facts, what room is there for the assumption that the solute is endowed with supernatural energy and is, in fact, behaving as an enclosed gas?

At the bottom of p. 9 Professor Porter says: "But the prime mover, or *causa causans*, of the whole disturbance seems indubitably to be the molecular agitation of the solute, and a knowledge of this provides us with the only way in which the value of the pressure has been calculated from theory." I am sorry Professor Porter had not time to read my contribution to-night. It is a rather striking thing if you compare his table on p. 12 with my table on p. 34, which show the difference between the observed and calculated values. My values are not only equally close, but they are even closer than Professor Porter's, and there is one remarkable thing about them. There is no available constant in calculating from my formula—it is absolute; whereas Professor Porter has this available constant b in the expression $P(v - b)$, and that enables Professor Porter to make the bottom figures correspond.

Professor Porter: Is not n in your expression an available constant?

Mr. Bousfield: No; n is taken from Morse's freezing-point values. One simply takes Morse's freezing-point values and calculates n from them, and then, having got n in that way, one calculates out the value of P.

Dr. Shorter: Are you not there simply verifying the laws of thermodynamics?

Mr. Bousfield: You may regard it as that. I have not time to read what I say about it, but I have put it very closely in the paper, and you can follow it from that. What I want to point out is that the values of n are deduced from the freezing-point values and there is no constant used at all, whereas with Professor Porter the agreement is not so close, and yet he has an available constant to play with. I think, therefore, that Professor Porter ought to withdraw his statement that that is the only way in which the value of the pressure has been calculated from theory. But further than that, Professor Porter only calculates it up to a normal solution. I have taken Lord Berkeley's values for the most concentrated solutions, and at the bottom of p. 34 you will see that I have calculated n from P, which is the same thing reversed. You will see that the series of the values of n agree right through the range of concentrated solutions and complete the series given at the top of the same page. It is even more striking when one comes to the case of electrolytes, but I will not follow that through to-night. On p. 36 of my paper the values of n are given from the freezing-point data and the vapour pressure data, and these values come out practically the same whether you get them from one or the other.

One more observation. On p. 13 Professor Porter gives some extraordinary values of n, going up to 53 molecules. He points out that "the values obtained for dilute solutions at low temperatures seem surprisingly large, but I am not aware of any argument which makes them impossible." I should like to point out one thing which does make them impossible. Here are the values of the viscosity of sugar according to Grüneisen :—

m	η_{18}	$\frac{\eta - 1}{m}$
0·2	1·208	1·04
0·05	1·046	0·93
0·02	1·018	0·90
0·01	1·009	0·90

so that the equivalent viscosity increment hardly varies at all in passing from $m = 0·2$ to $m = 0·05$. Therefore it is impossible, seeing that the equivalent viscosity increment is the same, that there could be that enormous variation in the number of molecules of water. The molecules of water must form some sort of aggregate, and if they form an aggregate in proportion to the water it would make an enormous change in the viscosity as between 0·2 normal solution, for which Professor Porter gives 15 molecules, and 0·1, for which he gives 53, whereas the variation of the viscosity increment is so small that there should not be any material change in the radius of the aggregate molecule as between these two.

Sir Oliver Lodge : I should like to ask one question, but if it cannot be answered briefly, do not answer it, because I may not be putting it quite right. With regard to that equation (p. 38), need you have gone into n at all, because are you not really calculating from the freezing-point?

Mr. Bousfield : It is not easy to answer it shortly.

Sir Oliver Lodge: If you get n from the freezing-point, virtually you are working back from the freezing-point.

Mr. Bousfield : One can calculate osmotic pressure accurately by using the values of n given either by freezing-points or vapour pressures.

Dr. Shorter : Supposing you had n^{-4}, you would have got exactly the same agreement.

Mr. Bousfield : No.

Sir Oliver Lodge : At all events, the answer is in the negative to what I ask.

Mr. Bousfield : If you read it, I think it is fairly explained in the paper. The point is that you can get values of n independently from conductivities, from vapour pressures, from the osmotic pressures, and from the freezing-points, and that you will then find them all concordant and expressible by the relations—

$$\frac{\mathrm{P}}{\mathrm{R'T}} = \frac{\delta p}{p} = \frac{\Delta}{\mathrm{F'}} = \frac{i}{h - n}.$$

Dr. S. A. Shorter (Leeds University) : My remarks on the subject of discussion may be arranged under the three headings—

1. The Kinetic Theory of Osmotic Pressure.
2. The Theoretical Basis of the Theory of the Ideal Dilute Solution.
3. The Theory of the Concentrated Solution.

1. *The Kinetic Theory of Osmotic Pressure.*

I propose to consider in this section the kinetic theory of the bombardment pressure produced by the solute molecules on the osmotic membrane. Professor Porter upholds the view that the osmotic pressure difference is produced entirely by the solute molecules, the bombardment pressure of the solvent in the solution being equal to that of the pure solvent. I apply the kinetic theory in a manner similar to that adopted by van der Waals in dealing with simple substances, and arrive at the conclusion that no such equality between solute bombardment pressure and osmotic pressure is to be expected, and that the relation between the two pressures will depend upon the nature of the intermolecular forces.

We will start from the virial theorem, which states that for a system of particles in a closed space

$$\text{Mean value of } \Sigma\tfrac{1}{2}mV^2 = -\text{ mean value of } \tfrac{1}{2}\Sigma(Xx + Yy + Zz),$$

where m is the mass of a particle; V its velocity; x, y, z its co-ordinates; X, Y, Z the components of the force acting upon it—the means being time-means taken for a period long compared with the period of the irregularities of the motion of the particles. Let us apply the theorem to the solute molecules in a dilute solution. We may divide the virial (as the right-hand side of the above equation is called) into two portions : (1) that arising from forces exerted by the walls of the containing vessel; (2) that arising from the forces exerted by the solvent molecules. The first portion may readily be proved to be equal to $3pv/2$, where v is the volume of the solution and p the solute bombardment pressure. Let us denote the latter portion by W. Then we have—

$$pv = \tfrac{1}{3}\Sigma mV^2 - \tfrac{1}{3}W.$$

The first term on the right-hand side is equal to the product of the osmotic pressure P and the volume. Hence, writing $w = W/v$, we have the relation –

$$p = P - \tfrac{1}{3}w$$

connecting the solute bombardment pressure and the osmotic pressure. This equation shows that the two pressures are equal only when the virial of the intermolecular forces is zero. This condition is fulfilled in the case of an ideal gaseous mixture, but not necessarily in any other case. In the case of liquid mixtures w may be either positive or negative. We may write—

$$w = a - r,$$

where a is the positive portion of w which arises from the attractive forces between the solute and solvent molecules and $-r$ the negative portion which arises from the repulsive forces operative during impact. If the attraction between a solvent and a solute molecule is not much less than that between two solvent molecules and the total pressure on the solution not very great, a will be less than r, and the solute bombardment pressure will be less than the osmotic pressure. If the force of attraction between the two kinds of molecules is very small, the bombardment pressure will exceed the osmotic pressure. In any case, by variation of the total pressure it is possible to make the total virial either positive or negative, and consequently p either less than or greater than P.

Putting the above argument in a form similar to that adopted in the popular exposition of van der Waals' equation, we may say that the free space in which the solute molecules move is much less than the total volume of the solution, owing to the large space occupied by the solvent molecules. In the absence of attractive forces between solvent and solute molecules, the solute bombardment pressure would therefore be enormously greater than the osmotic pressure. Attractive forces will, however, make the pressure less, and unless the forces acting on the solute molecules are much less than those acting on the solvent molecules, the bombardment pressure will be less than the osmotic pressure. Equality between the two will only be a coincidence, occurring when the force of attraction and the free space in the solution have suitable adjusted values.*

2. *The Theoretical Basis of the Theory of the Ideal Dilute Solution.*

As I have just shown, the kinetic theory of liquids leads us to the conclusion that the bombardment pressure of the solute is in general different from the osmotic pressure. Hence the "gas law" of osmotic pressure cannot be regarded as a satisfactory basis for the theory of the ideal dilute solution. We must start from some law whose kinetic explanation is immediately evident. This law is Henry's law, which states that in a dilute solution the partial vapour pressure of the solute is proportional to the concentration. The kinetic explanation of this law is quite simple. In a dilute solution a "sphere of action," drawn round a solute molecule, will practically never include within it another solute molecule. Hence the field of force in which each solute molecule moves will not vary with the concentration. Hence the rate of escape of the solute molecules into the vapour phase, and therefore the partial vapour pressure of the solute, will be proportional to the concentration.

Henry's law may conveniently be expressed thus—

$$\Pi_1 = kc_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where Π_1 is the "reduced partial vapour pressure" of the solute (i.e. the ratio of the partial pressure to the vapour pressure of the pure solute), c_1 the "molar fraction" of the solute, and k a constant (or, more precisely, a function of the temperature). The equation has two advantages over either the "gas law" or Raoult's law as the basis for the theory of the ideal dilute solution: (1) it is deducible from simple kinetic considerations; (2) it contains a term k dependent upon intermolecular forces—if the forces acting on the solute molecules are small, k is large; if large, k is small. This second advantage is of great importance, since it emphasizes the fact that intermolecular forces play a part even in dilute solutions.

The transition from the partial pressure of the solute to that of the solvent may be made by means of the well-known Duhem-Margules equation—

$$\frac{d \log \Pi_1}{d \log c_1} = \frac{d \log \Pi_0}{d \log (1 - c_1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which Π_0 is the "reduced partial pressure" of the solvent. Substituting the value of Π_1 given by equation (1) and integrating, we obtain the equation—

$$1 - \Pi_0 = c_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

---

* A similar coincidence occurs with a highly compressed gas. When the gas is first compressed from an approximately "ideal" state, the product pv decreases. At higher pressures pv begins to increase, and for a particular pressure reaches the "ideal" value. At this point the "impact term" and the "attraction term" of the virial just neutralize each other. At still higher pressures the "impact term" predominates.

which expresses Raoult's law, and from which the "gas law" of osmotic pressure may readily be deduced thermodynamically.

The "solute bombardment theory" does not therefore, as Professor Porter implies, provide the only way in which the "gas law" can be deduced from theory. It is true that the above exposition does not provide a direct kinetic explanation of the "gas law," but there is nothing surprising in this. It is only one of the many instances of simple relations deduced thermodynamically which have not received quantitative kinetic explanation. Such a state of affairs is simply a tribute to the tremendous power of the thermodynamical method, which achieves results whose validity is independent of any theory of the interior mechanism of the process under consideration.

3. *The Kinetic Theory of the Concentrated Solution.*

The fact that the ordinary osmotic theory of the ideal dilute solution pays no attention to the part played by intermolecular forces has led many investigators to ignore these forces even in concentrated solutions, and to put forward theories of the chemical structure of such solutions, based on the deviation of the solution from some assumed normal mode of variation, with concentration, of the thermodynamical properties. Such a mistake would never have been made, had sounder views on the theory of the ideal dilute solution been prevalent.

Let us consider what the kinetic theory of liquids teaches us with respect to the thermodynamical properties of concentrated solutions. As in the previous section, let us consider the partial vapour pressure of the solute. In dilute solution it will be proportional to the concentration, for the reason explained in the previous section. Let us consider the case in which the forces holding the solute molecules in the dilute solution are much less than those holding them in the pure solute (which we will assume to be a liquid). This means that k will be much greater than unity (as is generally the case). If the reduced partial pressure be plotted against the molar fraction, the curve will rise steeply from zero. As the concentration increases a point will be reached when the solute molecules will encroach on each other's "spheres of action." The force holding the solute molecules in the solution will be increased and the curve will become less steep. The steeper the initial rise, the more marked the subsequent flattening. If the rise is very steep the partial pressure will become equal to the vapour pressure of the pure solute at a comparatively low concentration. If this is the case, the increased attraction produced by increase of concentration will at a certain stage more than counterbalance the effect of the increased number of the solute molecules, so that the partial pressure will actually decrease with the concentration, till the rapidity of change of the field of force diminishes, and the effect of increased crowding of the solute molecules again predominates. We thus get a region of instability, i.e. the liquids are only partially miscible. The molecular forces may be so adjusted that very slight changes may determine whether there shall, or shall not, be this region of instability. The determining factor may be the effect on the molecular forces of a change of temperature—hence the phenomenon of the critical solution temperature. On one side of the critical temperature we have partial miscibility, on the other side, though there is perfect miscibility, the change is foreshadowed by a prolonged flattening in the partial pressure curves of the two components, indicative, so to speak, of a prolonged struggle between the two effects, change in the field of force and increased crowding of molecules, in which the latter just manages to be the victor.

It is evident that molecular forces are capable of explaining peculiarities of the most marked kind in the mode of variation with concentration of the vapour pressure (and therefore osmotic pressure) of solutions, and that the "ideal concentrated solution" is a fundamentally unscientific concept. There is, of course, nothing wrong in calling a solution with certain properties (say, one in which the reduced partial pressures of the components are equal to the respective molar fractions) an "ideal concentrated solution"; but to ascribe deviations from this ideal to some species of chemical action is absolutely erroneous.

From a logical point of view we may say that all the theories of the chemical structure of concentrated solutions are *ad hoc* hypotheses, which not only fail to explain anything but the one fact they were invented to explain, but which are contrary to the already existing body of knowledge on the subject. Professor Porter's theory of the hydration of the sugar molecule in aqueous solution is in even a worse logical plight. It is a second *ad hoc* hypothesis put forward to explain the failure of a previous *ad hoc* hypothesis. The hypothesis of an ideal concentrated solution having the properties implied in the equation—

$$P(v - b) = RT$$

(which has no *a priori* justification) is found to disagree with experiment, so a second hypothesis, that of hydration of the solute molecules, is put forward to explain the discrepancy.

With respect to Mr. Bousfield's theory as to the constitution of aqueous solutions, it may be pointed out that the numerical agreement he obtains between the values of the quantity n obtained from different experimental data is no proof of the correctness of the theory, but is simply a verification of purely thermodynamical relationships. To put forward such agreement as evidence in favour of the theory is just as fallacious as putting forward the agreement between values of the degree of ionization calculated respectively from freezing-point data and from vapour pressure data as evidence in favour of the theory of electrolytic dissociation.

The Earl of Berkeley, F.R.S.: I have only two remarks to make. I would like to point out one little difficulty in the internal vapour pressure method. If you take a column of concentrated sulphuric acid the vapour pressure is practically nil. If you put a layer of potassium bichromate at the bottom you will see that diffusion takes place at an appreciable rate. Diffusion on the internal vapour pressure theory is due to the vapour pressure of the two substances in some way or other, but how can diffusion take place? That would be one of the main objections. I also want to ask Professor Porter whether he can give me some idea of the accuracy of the latent heat method of measuring osmotic pressure. What concordance is there? With the vapour pressure method the concordance is about 1 in 800.

Professor J. C. Philip: I have only two points that I should like to raise. The first matter is a point in Dr. Tinker's paper with regard to the function of the membrane. He has adopted the view that a copper ferrocyanide membrane, to take a special case, is characterized by a porous structure, and he has studied the size of the particles which form the membrane and the size of the interstices between the particles. The work, however, although of great interest and value, may give a misleading impression in one respect. For Dr. Tinker, though starting from the conception of the membrane as a porous structure, finally comes to the conclusion that its action really depends, as I think has been recognized for a considerable time, on selective absorption by the substance of which the membrane consists, and that only in virtue of this differentiating action is it able to sift out the particles of the solute from those of the solvent.

In this connection a little difficulty occurs to me which, so far as I am aware, has not been discussed. The diameter of the pores of the membrane is, as Dr. Tinker has found, many times larger than the diameter of the crystalloidal molecule, so that if the pores acted simply as physical apertures there should be no difficulty in sugar molecules passing through. The view taken, however, is that the material lining the pores has the power of absorbing water preferentially, and that this adsorption of water renders the passage of the sugar impossible. But why should it prevent the passage of the sugar? Even adsorbed water, one might expect, should retain the power of dissolving sugar, in which case the membrane would allow sugar to leak through. Lord Berkeley's experiments, however, have shown that a copper ferrocyanide membrane can be prepared which will stand 130 atmospheres without leaking. In this case, at least, it is clear that the pore theory, pure and simple, does not apply, and we are thrown back on the factor of selective absorption, as Dr. Tinker says. There are cases, however, where the pore theory appears to be applicable. Reference may be made in this connection to the work of Berchhold, from which it seems that the power of membranes to sift out one kind of colloidal particle from another does depend directly on the size of the pores.

The other point concerns the question of the hydration of sucrose. Mr. Bousfield has alluded in his paper to some figures for the average molecular hydration which I tabulated ten years ago, these figures being based on the effect of sucrose in lowering the solvent power of water for gases. He thinks that these values are rather too high, whereas Dr. Porter in his paper arrives at values which, for the most dilute solutions at least, are somewhat higher than the figures indicated as probable by my calculations. In this connection I should like to mention that some recent work carried out in my laboratory on the partition of ethyl-acetate between sugar solutions and benzene gives values for the average molecular hydration of sucrose higher than those previously accepted as probable—from 11 for dilute solutions down to 6 or 7 for concentrated solutions.

Dr. G. Senter (*partly communicated*): I have for some years been a believer in the explanation of osmotic pressure based on kinetic considerations, and am in substantial agreement with the arguments in the section of Dr. Porter's Paper headed "The Kinetic Theory of Osmotic Pressure." The conception on p. 8 of an ideal solution in which the solute consists of massive points is very useful, as it affords a simplified picture of the possible mechanism of osmotic pressure which is readily grasped. The argument as a whole, however, would have been more convincing if some attempt had been made to meet the difficulties arising from the fact that in actual solutions molecular attractions and the finite volume of the molecules of the solute become of great importance. This appears the more necessary because, as shown below, considerable progress in the discussion of these points has already been made by previous workers.

In the section "An Interpretation of Experimental Results," Dr. Porter shows that the experimental data on osmotic pressure can be represented fairly satisfactorily by the modified van der Waals equation $p(v - b) = RT$. He has, however, overlooked the fact that the same formula was applied some years ago by Sackur * to the osmotic pressure data of Morse and Frazer for cane sugar, and was used at a still earlier date by Bredig and others. As

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* *Zeitsch. physikal. Chem.*, 1910, 70, 447; also *Thermochemie und Thermodynamik*, p. 221.

Sackur's calculations are based on earlier and less accurate data of Morse and Frazer, his values of v do not quite agree with those of Porter, but Sackur also finds that v diminishes rapidly with rise of temperature, and ascribes this to diminishing hydration of the solute.

Although Porter does not explicitly indicate the theoretical basis of the formula in question, this has already been done to some extent by Bredig and by Nernst, and I give the argument in the words of Sackur:[*] "Bredig[†] was first in pointing out that the force of attraction which the solute molecules exert on one another and which tend to counteract the dilution (and hence the osmotic pressure) are compensated or perhaps exceeded by the attraction between solvent and solute which favours the process of dilution and therefore increases the osmotic pressure. It is therefore probable that the correction for the molecular attraction is small enough to be neglected in moderately concentrated solutions. According to Nernst,[‡] it is necessary to take into account the volume of the solute molecules alone, while the correction for the volume of the solvent molecules can be disregarded. Hence, in moderately concentrated solutions, the osmotic pressure is represented by the equation $p(v - b) = RT$, in which b is four times the actual volume of the solute molecules and v is the volume of the solution which contains 1 mol of the solute." As Dr. Porter is an authority on gas equations, it would be interesting to have his opinion on the validity of the deduction just given.

The least convincing part of Porter's Paper is his calculation (p. 12) of the average hydration of the sugar molecules from osmotic data. As the value of b which fits the formula at 20° is 0·310 litres/mol, he assumes that the difference between this value and that of a gram-molecule of sugar (0·214 litres/mol) is due to hydration of the solute, and proceeds to calculate the average hydration of the sugar molecules on this basis. There is no evidence, however, that the true value of b in the absence of hydration would correspond with the volume of the solute at that temperature, nor is there any evidence that 0·214 litres/mol is four times the actual volume of the sugar molecules (in the sense of van der Waals' equation). Further, the variation of the hydration numbers with dilution (p. 13) in some cases appears difficult to reconcile with the law of mass action. It was shown long ago by Nernst that when the solute combines with the solvent, according to the equation $S + n . H_2O \rightleftarrows S(H_2O)n$, the ratio of the hydrated to the non-hydrated solute must be practically constant in relatively dilute solution, since under those circumstances the "active mass" of the water on the left-hand side of the equation scarcely varies with further dilution. Assuming, as usual, that the active mass of a solvent is proportional to its vapour pressure, I find that the active mass of the water increases by about $\frac{1}{500}$ of its value in passing from a 0·2 molar to a 0·1 molar solution, whilst, according to the table of hydration numbers (p. 13), the hydration at 0° increases within these limits from 15·8 to 53 molecules per molecule of sugar.

These "hydration numbers" unfortunately cannot be checked by any independent method, as hitherto no satisfactory method of measuring hydration in solution has been discovered. The fact cited on p. 12, that the method under discussion and a different line of argument used by Callendar both indicate that under certain conditions sugar molecules are associated with about 5 molecules of water does not help matters much, as Dr. Porter proceeds to point out what appears to be a fatal objection to Callendar's formula. There is little doubt that the phenomena under consideration are due to some extent to changes of hydration, but, as Morse points out,* it is necessary to know more about the osmotic pressures of aqueous solutions of other substances than cane sugar before the question of hydration, from the quantitative standpoint, can be discussed with any confidence.

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[*] Loc. cit.

[†] *Zeitsch. physikal. Chem.*, 1889, 4, 447.

[‡] *Lehrbuch*, 1st edition, p. 193.

The applicability of modified forms of van der Waals' equation to represent the results of osmotic pressure measurements has also been considered by Lord Berkeley and Hartley,† but these observers have not discussed in detail the theoretical significance of the equations used.

Dr. T. Martin Lowry, F.R.S. : Dr. Senter's criticism of the figures given by Professor Porter for the hydration of cane-sugar in dilute solutions may be corroborated by looking at the figures in another way. Thus, at 0° C., one molecule of sugar is stated to combine in decinormal solution with 53 mols of sugar, and in 0·2 N solution with 15·8. This means that in presence of 1 molecule of sugar 10 litres of water contain 53 mols combined, but in presence of 2 mols of sugar only $2 \times 15{\cdot}8 = 31{\cdot}6$ mols, i.e. increasing the total amount of dissolved sugar actually decreases the total amount of combined water. This is a contradiction of the laws of mass-action analogous with a suggestion which was once put forward that the hydration of a dissolved salt could be diminished by dilution.

Mr. W. C. Dampier Whetham, F.R.S. : I should like to make one point which I felt sure somebody else would have made, namely, to amplify what has been said with regard to the thermodynamic theory. While it enables us to predict the theoretical value, which is confirmed by observation of the actual osmotic pressure, and to work out the different relations between the osmotic phenomena and the vapour pressure and the freezing-point, it does not enable us to decide at all as to the mechanism by which the osmotic pressure is produced. I have a feeling that the expression which Mr. Bousfield put on the board was really only another way of verifying one of the relations between the osmotic pressure and the freezing-point. That is to say, as somebody else mentioned, it was simply a verification of one of the thermodynamic relations. What we have got to do, in order to get a satisfactory theory of the mechanism of osmotic pressure, is to begin quite afresh independently of thermodynamics, and predict the actual value of the pressure from first principles. Probably the kinetic theory is, as has been said, the only one which has yet been put forward which enables us to do this. My own instincts are rather in favour of the chemical theory, but, as far as I can see, there has been no chemical theory put forward which, like the kinetic theory, really does predict the actual and observed values for the osmotic phenomena.

Sir Oliver Lodge : It will be convenient if at this stage Professor Porter will reply to the criticisms that have been made on his Paper. That will not necessarily close the discussion.

Professor Alfred W. Porter : It is very difficult to reply in a few minutes to all the remarks that have been made, and I am afraid that the greater part of the reply will have to be left to be communicated, and will appear in print later. But there are one or two points that I might mention now. The difficulty which Mr. Bousfield has in seeing how it is that the pressure on the surface of the vessel in which the solution is contained, or the pressure on the surface between it and the vapour, can be so exceedingly small, is really a very simple matter. Any remarks that I make now are applicable not only to the surface of the vessel or to the free surface, but also to the semi-permeable membrane which exerts a counteracting force preventing diffusion of the molecules. The reason the vapour pressure of the sugar molecules is not equal to the osmotic pressure is because the solute molecules, as soon as they come near the surface, are drawn downwards by the attractive force of the molecules of the solvent, and, in the case of a non-volatile solute, none of them ever succeed in escaping from the surface. The amount that they contribute to the total pressure inside may be equal to the gas pressure, while the pressure they contribute outside is nothing. At the surface of the vessel pictured by Mr. Bousfield the same kind of thing comes into play. Inside, the pressure is that due to the gas bombardment; the pressure contributed outside may be anything—even quite small compared with the other. The same remarks apply to the semi-permeable membrane, although believers in the gas theory often do not realize this. The difference between a semi-permeable membrane and the rest of the surface of the vessel is that in the former there are canals through which the solvent can pass while the solute cannot. It might at first sight be expected that the pressure there might be different from that upon the rest of the vessel. But in order that differential and selective treatment shall be given to the two kinds of molecules, these canals must be so narrow that the mechanical forces that arise inside the canals arise mainly from the action of molecules that lie outside them. In other words, their diameter must be small compared with the range of molecular action, and the motion of the sugar is controlled not only by the forces in the water but by the forces that exist in the colloidal part of the membrane. If the canals were large in proportion to the range of molecular action, that statement would be no longer true, but then such a state of things would not give you a semi-permeable membrane. I do not think I have made that very clear, but I will put it more clearly when I get it into writing. The difficulty may be stated in the following way. If the same state of things exists at this membrane as exists at the free surface of the solution, and if it is true that the molecules of the solute never probably succeed in reaching the membrane, how is it that there is a pressure due to them at that point at all? If I strike a piece of paper lying on the table, I am acting on the table as much as if the paper were not interposed. I am exerting a force upon the table through the thin film of paper, and it seems to me to be perfectly legitimate to speak of that as a bombardment upon the table. You can calculate it by calculating the effect exerted by my hand, or no doubt you could calculate it by aid of a more minute examination of the conditions existing in the thin surface of separation, and the same two courses are open to you in dealing with the action of the solute and the semi-permeable partition. I think possibly this removes one of the objections which have been urged against the simple molecular theory as an explanation of osmotic pressure. Let it be granted that there is a thin film that is never penetrated by the solute, and yet the actual force which the partition experiences is directly due to the fact that there is a bombardment by the solute at the back, and in the case of dilute solutions it is most simply calculated from that fact.

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* Morse, Holland, Zies, Myers, Clark, and Gill, *Amer. Ch. J.*, 1911, 45, 603.

† *Proc. Roy. Soc.*, 1907, 79, A, 125.

I am rather inclined to leave all the other questions. I do not think I can properly deal with them until I have seen them written out in detail, so that I can get to know exactly what some of them mean. I am afraid I cannot answer at present the question that Lord Berkeley put as to what concordance is obtainable from the method of using the latent heat of dilution for determining osmotic pressures, but it is a very considerable accuracy.

I am quite pleased if the vapour pressure method is near it in accuracy. I have got a certain parental interest in that method when applied to strong solutions, and it is very satisfactory to hear that the accuracy is as high as 1 in 800. I hardly think the latent heat method is as high, and it has one drawback—that in order to apply it it is necessary to know the osmotic pressures at one definite temperature. It is a differential effect that is measured, so that it only gives you the rate of change; the vapour method is free from that drawback. I will look into the question of the accuracy.

Professor T. S. Moore: In Professor Porter's paper the cause of osmotic pressure is given as the molecular agitation of the solute, the effect produced by this agitation being modified in concentrated solutions by the attractive force and volume of the solute molecules, or of the complexes with solvent molecules formed by them. A slight reference is made on p. 8 to the forces exerted by solvent molecules on solute molecules, but in the rest of the paper these forces are neglected, and no reference is made anywhere to the effect of the volume occupied by the molecules of the solvent.

Now, if we wished to deduce from the kinetic theory an expression for the partial pressure of a gas A in a mixture of two imperfect gases A and B, existing under compression (the gases being in the proportion of 1 molecule of A to 60 of B—roughly the proportion of sugar molecules to water molecules in a normal solution), we should have to take into account (*a*) the volume occupied by the molecules of both A and B, (*b*) the forces exerted by A molecules on A molecules, and (*c*) the forces exerted by A molecules on B molecules. Under a small total pressure it is possible that the effects of all these factors will be negligible; and it is possible that the compression would have to be considerable before the effect of the second factor need be considered. But it is certain that (1) as soon as the volume of the molecules has to be taken into account at all, the volumes of both A and B molecules must be considered, and not the volume of the A molecules alone; and (2) the third factor must be taken into account as soon as the region of pressures is reached where for either gas alone the attractive forces of the molecules have an appreciable effect. It does not seem reasonable to suppose that if the total pressure of the mixture is high—200 or 300 atmospheres—the partial pressure of A, as determined by a piston permeable to B alone, would be independent of the volume of the B molecules and of the forces exerted by A molecules on B molecules. Now, since the internal pressure of a solution is measured in thousands of atmospheres, i.e. the molecules are much more closely packed than in the mixture of gases dealt with above, it seems impossible to suppose that the pressure exerted by the solute molecules on a membrane permeable to solvent alone can be independent of the volume of the solvent molecules and of the forces exerted by the solute molecules on the solvent molecules, no matter how dilute the solution may be; yet, if I have not misunderstood Professor Porter's paper, these are the assumptions he makes. And it is to be noted that the force thus neglected—the force exerted by the solvent on the solute—is the force to which the production and maintenance of the state of solution are primarily due.

It is certainly true, as Professor Porter points out on p. 8, that much of the difficulty of the problem of osmotic pressure is removed if we consider molecules as massive points and neglect their actual extension in space and mutual attractions. But if we can do this for a highly condensed system such as a solution, all the more ought we to be able to do it for a comparatively rarefied system, such as a gas under 200 or 300 atmospheres pressure. Actually, we know that to represent the behaviour of a gas at such pressures it is necessary to take into account both volume and attractive forces.

Since osmotic pressure is only one of the many effects produced in a solvent by introducing solute, a molecular theory of osmotic pressure cannot in reality be distinct from a general molecular theory of solution. Whatever molecular mechanism is assumed for the explanation of osmotic pressure must be capable of explaining all the effects (such as lowering of vapour pressure, change of volume, change of surface tension, etc.) produced by the addition of solute. It seems, then, that a theory of osmotic pressure that neglects properties of the molecules on which these effects must depend can have little real meaning, even if it succeeds in producing formulæ for osmotic pressure which approximately reproduce the experimental values.

Sir Oliver Lodge: It is getting near the time when we should stop, but I should like to say a few very elementary things, suggested partly by Mr. Bousfield's criticism. One must remember that in dealing with liquids we have, in addition to the external pressure which in a perfect gas is the only pressure, what we call the internal pressure also, which is enormous, and which maintains the liquid state.

In the ordinary equation $(p + K)(v - b) = RT$, it is that K, the internal pressure, the cohesion pressure, the mutual attraction of the molecules, which prevents the external pressure from being anything big. The external pressure on Mr. Bousfield's tumbler, for instance, is small owing to the K, which is big. I also want to ask whether every one will agree with this statement. Suppose you have a vessel like a closed tube or cylinder, and you fill it completely with water, and then put a semi-permeable membrane across it: we have done no harm to the water; the water is as it was before. Everything is in equilibrium. Now I am going to add sugar on one side. How can I get it in? What room is there for the sugar? It must produce an increased pressure. The water is in equilibrium, as before, but the sugar exists as an extra on one side of that semi-permeable membrane. The bombardment of its molecules is added to the bombardment of the water molecules. Does everybody agree with that?

Dr. Porter: It is a question of the consequences that follow. What are the consequences?

Sir Oliver Lodge: The consequence is that you have more pressure on the sugar side than on the other, and that this excess is, roughly and subject to details, the osmotic pressure. [I agree with Mr. Bousfield that the water molecules are more active, but they are on both sides and adjust themselves into equilibrium, allowing for changes of volume and other details, whereas the sugar is an extra, on one side only.]

Lord Berkeley: It depends on the change of volume what the pressure would be.

Sir Oliver Lodge: The main fact is that the sugar cannot get through that semi-permeable membrane, therefore it must cause extra pressure. The extra pressure is produced gradually by osmosis in the ordinary case. When sugar solution is put on one side, and water on the other, initially at the same pressure, the water diffuses through the membrane until equilibrium as regards water is attained; i.e. until the state of things is attained which I assumed to start with.

Mr. Bousfield: If you put a little soda inside it will attract, yet the osmotic pressure for soda would be as great as for sugar. The water plus soda will occupy less space than water alone.

Sir Oliver Lodge: Is not the difference between soda and sugar because soda, being an electrolyte, goes through more easily?

Mr. Bousfield: There will be spaces between the membrane and the solution. It will try to take up these because it destroys so many molecules and makes the whole thing smaller.

Dr. Porter: The Chairman means that the sugar is put in and yet the total volume of the water remains the same. There would be shrinkage whether it was sugar or soda.

Mr. Bousfield: You would look fcr a change of volume.

Dr. Porter: The Chairman has taken the case of a quantity of water and sugar—say a litre of water and a c.c. of sugar—and it is still to occupy one litre. To do so its pressure must become high, and the question is, Is that additional pressure equal to the osmotic pressure? I do not think it is, but I think it would approximate to the osmotic pressure in the particular case of an ideal kind of sugar which I recommend you in my Paper to take—a kind whose molecules have no volume. It is in reality, although that point is often neglected, only for the case in which the molecules of the dissolved body are merely moving points that the gas rule for calculating osmotic pressure holds good. You have a litre of water and a molecule of ideal sugar, and you do not increase the volume of the water if you put the sugar in. The natural increase of pressure to keep the volume the same in spite of outward bombardment of the sugar molecules will be equal to the gas value.

Sir Oliver Lodge: That is what I thought. You are bothered only by b.

Professor Porter: Yes.

Sir Oliver Lodge: You have a water bombardment on both sides, and on one side you have the additional bombardment of the sugar. That is why I rather agree with Dr. Porter on the whole. That is why we rather attend to the sugar molecules in spite of their being less active. They are the something which is added to the water, and you get the extra bombardment of the sugar particles, for whatever it may be worth; and it seems to me to be approximately the osmotic pressure, subject to certain water adjustments and other necessary minutiæ. I cannot quite grasp your theory yet, Mr. Bousfield, but I will try to grasp it from the Paper.

Professor T. S. Moore: There seem to be two gas theories, but in this theory on which is based your simple illustration, the sugar molecules are supposed to behave as a perfect gas and as if water is not there, although it is. That is one theory, and it is one which it seems to me anybody who has studied the kinetic theory as applied to compressed gases cannot accept. On the other hand, there is the other kinetic theory, which, I take it, Dr. Porter supports.

Dr. Porter: I support this one (Sir Oliver Lodge's).

Professor Moore: I understood from your reference to Perrin's work that you were talking about a direct bombardment not only of the sugar molecules but of the water molecules.

Sir Oliver Lodge: I do not depend upon the substance behaving as a perfect gas. If sugar is very dilute it would be like a perfect gas, whereas in stronger solutions it behaves more like an imperfect gas; but still it is subject to gas theory, taking into account the interaction of the molecules themselves.

Professor Moore: But it seems to me that the modification of the gas theory to deal with this problem would have to be very fundamental. I think it ceases to be a gas theory entirely, and the calculation would have to be carried out rather according to the method necessary in dealing with the Brownian motion than by the methods used in dealing with gases. It seems to me that for any dilution of sugar you would have to use methods such as Perrin's, because sugar molecules are being bombarded all the time by water molecules.

Dr. Porter : Since you have to deal with the volume of the solute, that is quite true; and it is because of a recognition of that that I say that a deviation from the gas laws for osmotic pressure will not be identical with the deviation from gas laws for gases themselves. There are other things to be taken into account, and you must include them.

Sir Oliver Lodge : I am quite in agreement with that.

Lord Berkeley : I would like to point out that the curve of osmotic pressure is well known. In the van der Waals equation you have to deal with a curve for gases which goes one way and a curve for osmotic pressure which goes another way. K is a negative sign if you use van der Waals' equation. It makes a fundamental difference at once, practically.

Dr. Porter : That is why I chose, in estimating the value of b, provisionally to ignore K altogether.

Sir Oliver Lodge : I wondered why you did it.

Dr. Porter : When you take it into account it makes little b greater than before.

Mr. Bousfield : I have written a paper which I did my best to make closely reasoned. I have been hoping that somebody would point out some flaw in my reasons. Nobody has done so. I am afraid it is simply because there has not been time to read the paper.

Sir Oliver Lodge : Mr. Bousfield is anxious that some one should tread on the tail of his coat.

Mr. Bousfield : With regard to vapour pressure and sulphuric acid, that is a question of velocity. The vapour pressure is probably proportional to the number of steam molecules in the water. It is perfectly true of sulphuric acid, and you would probably have very much more vapour pressure from the bichromate solution because it would not be so concentrated as sulphuric acid. There is always some vapour pressure.

Lord Berkeley : But vapour pressure would be so small as to make it inconceivable that it takes any part.

Mr. Bousfield : It is not inconsistent with what we are saying. I wrote one passage on p. 38 of my paper: "Now the process of diffusion does no doubt involve the molecular activities both of the solute and of the solvent." There is no doubt that you have the solute molecules vibrating and the solvent molecules also, and all the facts tend to show that the activity of the vapour is vastly greater than that of the solute, and you can theoretically, thermodynamically, and in accordance with experiment, explain the phenomena by regarding the activity of the vapour as the chief factor and neglecting the activity of the solvent.

Sir Oliver Lodge : I think we can congratulate the Society on the discussion. I have tried to bring the opponents together, but I do not think I have succeeded. At any rate, it is a large subject which we cannot settle completely this evening,

Sir Robert Hadfield : I am sure you will not wish to part without expressing your hearty thanks to Sir Oliver Lodge for presiding this evening. He has come a long way, and we have had the advantage of his usual lucid remarks in throwing light upon a number of intricate problems. We have all listened with very great interest to the Papers and discussion, and have been very much instructed. I therefore propose a hearty vote of thanks to Sir Oliver Lodge.

The vote of thanks was unanimously accorded, and the proceedings terminated.

Communications to the Discussion received subsequent to the Meeting.

Dr. J. J. van Laar: As I have already often stated it, my point of view concerning osmotic pressure differs a little from the usual conceptions. I think the so-called "osmotic" pressure is only a consequence of the well-known phenomenon of diffusion. When water (of concentration $1 - x_1$) + sugar (conc. x_1) is in contact with pure water, for example, then the sugar molecules in the solution are no longer in thermodynamic (statistic-kinetic) equilibrium with those in the water (supposing that this contains a very little quantity x_2 of sugar) and will diffuse into the pure water. For the same reason the water molecules will diffuse in the opposite direction: from the pure water into the solution.

Now, it is easy to show that the diffusion-tension of the sugar molecules is proportional to $\log \frac{x_1}{x_2}$. When therefore $x_2 = 0$ (pure water), the diffusion-tension of the sugar into the water becomes logarithmic infinite, and not—as in the ordinary kinetic theories of osmosis—proportional to x_1. On the other hand, the diffusion-tension of the water molecules will be proportional to $-\log \frac{1 - x_1}{1 - x_2}$, that is to say, proportional to $-\log (1 - x_1)$, when $x_2 = 0$. Only *this* tension is, with small values of x_1, nearly proportional to x_1, the concentration of the sugar molecules in the solution.

A semi-permeable membrane between the solution and the water eliminates the diffusion of the sugar molecules and permits the free diffusion of the water molecules from the water into the solution. This diffusion can only be stopped when so much water has penetrated into the solution that the hydrostatic excess pressure (in the osmometer) of the solution will just compensate the diffusion-tension of the water. This opposite hydrostatic pressure, which is, therefore, a measure for the diffusion pressure of the water (directed from the water), is commonly called, improperly, the "osmotic" pressure of the solution.

As I remarked, the osmotic pressure can be calculated from thermodynamic principles, and in no way by ordinary kinetic theories. Only a statistic-kinetic theory (analogous to the theory of "Brownian" movements) would give the same results as the pure thermodynamic theories, as these special kinetic theories are the equivalent of the thermodynamic ones.

Equalizing now the molecular thermodynamic potentials of the water in the solution (under pressure p) and of the pure water (pressure p_0), we get:

$$\mu(x, p) = \mu(0, p_0),$$

where x and 0 are the concentrations of the sugar in the solution and in the water respectively. From this we have:

$$f(\mathrm{T}) + pv_x + \alpha x^2 + \mathrm{RT} \log (1 - x) = f(\mathrm{T}) + p_0 v_0.$$

In dilute solutions the molecular volume of the water in the solution (v_x) differs from that of the pure water (v_0) only by a quantity of order x^2 (which can be added to the term αx^2), so that it becomes:

$$\pi = p - p_0 = \frac{\mathrm{RT}}{v_0} [-\log (1 - x) - \alpha x^2].$$

The term ax^2 is due to the reciprocal action of the two substances in the solution. As I have often stated (e.g. in the *Zeitschr. f. Phys. Chem.*, 63, pp. 221 ff. and 227 ff. (1908)) the quantity a is given by

$$a=\frac{a_1b_2^2+a_2b_1^2-2a_{12}b_1b_2}{b_1b^2}=\frac{(b_2\sqrt{a_1}-b_1\sqrt{a_2})^2}{b_1b^2},$$

when $a_{12}=\sqrt{a_1a_2}$ (a and b are the well-known constants of the equation of state of van der Waals). As $b=b_1(1-x)+b_2x=b_1+(b_2-b_1)x=b_1(1+rx)$, the quantity a will be in general still a function of x. [The corresponding term in the expression for the molecular potential of the sugar in the solution can be got by substituting b_1 for b_2 in the denominator of the above-mentioned expression for a, and x by $1-x$ in ax^2.] In many solutions (particularly in mixtures of organic substances, where the critical pressures differ but little) a can be put $=0$, and then we find for the value of the (hydrostatic) excess pressure $\pi=p-p_0$ on the solution, which compensates the diffusion pressure of the water:

$$\pi=\frac{\text{RT}}{v_0}(-\log(1-x)).$$

All ordinary kinetic theories which give expressions with x alone (and, if corrected for deviations from the ideal gas state, give $v-b$ instead of v, etc., and not the combination of a's and b's as occurs in the above deduced expression for a) are, therefore, inexact. As I have shown,* the experimental results of Morse and Fraser † agree very well with the simple formula for π, deduced by me, which formula remains still valid even for great values of x.

Only in the case of very dilute solutions x can be put for

$$-\log(1-x)=x+\tfrac{1}{2}x^2+\ldots,$$

and then the above-mentioned formula passes into the van't Hoff expression $\pi=\frac{\text{RT}}{v_0}x$, which exhibits a (purely accidental) analogy to the "gas laws." But the analogy is only due to the thermodynamic (statistic-kinetic) term $-\log(1-x)$ of the so-called "paradox of Gibbs," which is the well-known expression for the diffusion-tendency of the water.

In the same way we would obtain for the sugar (neglecting the terms with a):

$$f(\text{T})+pv'_{x_1}+\text{RT}\log x_1=f'(\text{T})+p_0v'_{x_2}+\text{RT}\log x_2,$$

when the membrane is only permeable for the sugar molecules. Equalizing again the molecular volumes of the sugar $v'_{x_1}=v'_{x_2}=v'$, we get:

$$p-p_0=-\frac{\text{RT}}{v'}\log\frac{x_1}{x_2},\quad\text{or}\quad p_0-p=\frac{\text{RT}}{v'}\log\frac{x_1}{x_2},$$

when the "water" contains a little quantity x_2 of sugar. So we find that the osmotic tension of the sugar from the solution into the (nearly pure) water will be proportional to $\log\frac{x_1}{x_2}$, as I have stated above. This tension becomes infinite when $x_2=0$ (pure water). We should pay attention to the fact that *this* pressure has the *opposite sign* to the diffusion pressure of the water. The pressure p_0 on the (nearly) pure water should be greater than the pressure p on the solution, to stop the diffusion of the sugar from the solution into the water.

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* *Proc. Amsterdam*, June, 1906, pp. 53–63.

† *Amer. Chem. Journ.*, 34, pp. 1–99, 1905.

The diffusion pressure of the water (osmotic pressure) is then proportional to $-\log(1-x) = x + \ldots$ (in analogy with the gas laws); that of the sugar, on the contrary, proportional to $\log \frac{x_1}{x_2}$, and here all analogy with the gas laws vanishes—in complete opposition, therefore, to the ordinary osmotic theories.*

The so-called "osmotic" pressure never exists in an isolated solution. Only in the case where two solutions of different concentrations (or a solution and the pure solvent) are in contact, so that diffusion can take place (disturbed or not by a semi-permeable membrane), then the diffusion-tendency † appears and causes the diffusion pressure, e.g. the diffusion pressure of the water (in the case of a membrane, which permits the water molecules alone to pass), and of the opposite hydrostatic ("osmotic") pressure in the osmometer. That this conception is exact, is proved by the fact that the same "osmotic" pressure can be calculated in the case of a mixture of two ideal gases in contact with one of them, as I have remarked in my *Lehrbuch der Math. Chem.*, p. 72 (1901). And no one will speak here of a special "osmotic" pressure in the isolated mixture of the two gases, where the total pressure is, as usual, equal to the sum of the two partial pressures.

For further developments I refer specially to my last exhaustive article on this subject (controversy between Professor Ehrenfest and myself in the *Proc. Amsterdam*, June, 1915, p. 184 ff.), to my former papers in the *Zeitschr. für Phys. Chem.*, 15, p. 463 ff. (1894) and 64, p. 629 ff. (1908), in the *Proc. Amsterdam* of June, 1905, pp. 49–51, and to the *Sechs Vorträge*, pp. 17–36 (1906).

Professor A. Findlay: Since I was, to my great regret, prevented from attending the meeting of the Faraday Society at which the subject of osmotic pressure was reviewed and discussed, I avail myself of the Society's invitation to contribute to the discussion of this important question by sending these few lines in writing. Perhaps I may be allowed to emphasize how necessary it seems to me that in our treatment of the various problems and questions which arise around the central phenomenon we should keep quite clear in our minds the two essentially different matters, the equilibrium pressure and the process by which this pressure is produced. The process of osmosis and the rôle of the semi-permeable membrane are matters of the highest importance in certain connections, but are apparently

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* So, if the concentration x_1 of the sugar in the solution is, for instance, $= 0{\cdot}01$, and that (x_2) in the "water" $= 0{\cdot}0001$, the diffusion pressure of the water into the solution will be

$$= \frac{RT}{v_0} \times \left(-\log\frac{1-x_1}{1-x_2}\right) = \frac{RT}{v_0} \times (0{\cdot}01 - 0{\cdot}0001) = \frac{RT}{v_0} \times 0{\cdot}01 \text{ nearly};$$

while the corresponding pressure of the sugar into the water is

$$= \frac{RT}{v'} \times \log\frac{x_1}{x_2} = \frac{RT}{v'} \times 2 \times 2{\cdot}303 = \frac{RT}{v'} \times 4{\cdot}6 \text{ nearly}.$$

If now v' of the sugar approximately $= v_0$ of the water, then the diffusion pressure of the sugar will be as much as 460 times that of the water. And when $x_2 = 0{\cdot}00001$, then the proportion of the two pressures becomes 690; etc. That is to say, the pressure of the sugar would be $=$ 460 to 490 times the "osmotic pressure" of the solution.

† I am happy to see that this is also the meaning of Dr. Tinker, who says with full clearness (*supra*, p. 23): "It is my personal opinion that this supposed gas analogy is *not a real one*; it overlooks the facts of the fundamental *diffusion* phenomena altogether." And further on: "It is in the nature of the osmotic pressure that the pure solvent should flow *into* the solution." So it is, and this opinion has been stated by me for the last quarter of a century.

—one should not dogmatize on such a matter—of little, or comparatively little, importance in respect of the main problem of the numerical value of the equilibrium pressure and the relation of this to the concentration and constitution of the solution. The general thermodynamic relations between a solvent and a solution have, during the past ten years, been worked out pretty satisfactorily, and having now obtained these, what we now mainly require, I venture to think, is a satisfactory picture of the constitution of a solution. There is one other point which I have tried elsewhere to emphasize, but which is perhaps not sufficiently borne in mind, namely that it is unwise to identify, as Nernst does, osmotic pressure with the "expansive force" which brings about diffusion. In fact, I am of opinion that the term "osmotic pressure of a solution" is a bad one, because what we are really concerned with (I am thinking now of the equilibrium pressure relationships and not of the process of osmosis) is a definite physical quantity or property of the solution which is independent of osmosis and of membranes. It is for this reason that I have never been able fully to accept the kinetic treatment of the problem, in spite of the success obtained by Professor Porter and others. The weakness of the method appears to me to lie in the fact that, having adopted the general equation $P(v - b) = RT$, deviations from this are attributed solely to "hydration." No account, as Professor Porter points out, is taken of what we must certainly regard as existing—the association of water molecules with each other. A method of testing the values of osmotic pressure which appears to me to be preferable is that referred to by Professor Porter, the connection between heat of dilution and osmotic pressure. I had some time ago instituted some work in this direction, but it had unfortunately to be abandoned at an early stage owing to the war.

But we have still to obtain an explanation of the physical quantity known as osmotic pressure. Accepting the definition given by Professor Porter, one is at once led to think of a connection between osmotic pressure and the internal pressure. This idea was mooted by Tammann, who determined the change in the specific volume of the solution and then calculated the external pressure under which the pure solvent undergoes the same change in volume. This pressure he regarded as the inner pressure of the solution; and it seems plausible at least to regard this pressure as being equal to the osmotic pressure. On calculating the pressure values for different concentrations, however, one obtains numbers which are very much greater than the osmotic pressures. Quite recently, however, Shinkichi Horiba has determined the molecular solution volumes of both solvent and solute in a number of aqueous solutions, and he has found that with increasing concentration the molecular solution volume of the solvent diminishes. If one calculates the external pressure which would be necessary to effect such a volume change, numbers are obtained which are much less than Tammann's numbers, although still somewhat greater than the osmotic pressure values for concentrated solutions. For dilute solutions very fair agreement obtains. The conclusion is therefore drawn that the first cause of the osmotic pressure is the inner compression of the solvent in solution. The explanation is not yet complete, but further advance in this direction promises to afford much insight into the constitution of solutions and so allow of a more perfect understanding of osmotic pressure.

Mr. J. R. Partington: The fundamental assumption for the molecular theory is the equipartition theorem that the average kinetic energy of translation of a molecule must be the same at all parts of a system in equilibrium at a uniform temperature, and equal to $\frac{3}{2}kT$, where k is the fundamental gas constant. Thus, if we consider a *volatile solute*, the molecules of solute in the vapour space and in the body of the solution have the mean kinetic energy $\frac{3}{2}kT$, and therefore their contribution to molecular bombardment will be exactly the same. Therefore the average rate of contribution to the momentum gained by any imaginary plane, due to the one kind of molecule alone, will be the same no matter whether the imaginary plane is drawn in the gas space or in the solution, and this result, which depends solely on the kinetic energy, will be quite independent of the attractive forces which exist between the molecules of solvent and solute.

Hence, although the actual physical state of the dissolved molecules may not be comparable with those of the gaseous molecules, e.g. their free paths are different, yet they behave with respect to bombardment exactly as if they existed in the state of a gas. If, therefore, we imagine two sets of demons rigidly arranged on two parallel planes, one plane in the gas space and the other in the liquid, and if each demon could reverse the motion of each solute molecule projected in a direction perpendicular to the plane, say by striking the molecule with a perfectly elastic club or cricket bat, the reactions averaged over each plane would be equal for equal numbers of molecules. For the first reaction is the gas pressure normal to the surface, which is known to be

$$p = \tfrac{1}{3}\, mn' \, \overline{u^2}$$

where u is the velocity perpendicular to the first plane.

Similarly, the second reaction is the pressure

$$P = \tfrac{1}{3}\, mn \, \overline{U^2}$$

where U is the velocity perpendicular to the second plane.

But

$$m\overline{u^2} = m\overline{U^2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

and $\therefore p = P$ when $n' = n$, i.e. when the concentrations are equal.

If P is defined as the osmotic pressure, the relation follows at once. Equation (1) is a direct consequence of the experiments of Perrin, and is therefore independent of all hypothesis. It may, in fact, be used to demonstrate the validity of the equipartition theorem in this particular case.

It remains to be shown, however, that the ordinary osmotic pressure is in fact the same magnitude as P. For this purpose it is sufficient to remember that the magnitude p arising on the first surface is undoubtedly the gas pressure, and is equal to the partial pressure when the demons act selectively in a mixture of gas molecules. If the demons act also selectively in the liquid mixture, we have in their aggregate exactly the property postulated for an ideal semi-permeable membrane, and the reaction on such a membrane is defined as the osmotic pressure.

In the same way as we allowed the demons in the first plane to choose their implements for causing molecular reversals (e.g. they may use ideal cricket bats, or racquets, or clubs), so those in the second plane must have an equal freedom of choice, which is equivalent to the statement that the osmotic pressure is independent of the nature of the semi-permeable membrane, provided the latter fulfils its function completely.

The question as to whether the osmotic pressure is "caused" by the solute or by the solvent appears to be largely meaningless. Thus, the well-known experiment of Ramsay has been used by the supporters of both schools of opinion, with the result that in the one case the pressure increase is referred to the entering hydrogen (solvent theory), in the other to the nitrogen originally present in the palladium bulb (solute theory). In each case the conclusion appears perfectly justified. The following experiment also leads to interesting considerations. Let us suppose we have a non-volatile solvent contained in a semi-permeable pot, and enclosed in a vacuous enclosure screened from the influence of gravity, say by carrying out the experiment at the centre of the earth. The pressure on the inside of the pot is zero. If we enclose the solvent by a piston, and apply an infinitesimal pressure δP to the piston, the solvent will ooze through the membrane, and if the pressure is maintained, the whole of the solvent will pass through. Can δP be reduced indefinitely, i.e. is the pressure due to the solvent zero? Evidently, when the irreversible phenomenon of viscosity in the pores of the membrane is neglected, i.e. if we consider an ideal membrane, δP may be regarded as approaching zero, and, in fact, if we subject the liquid inside to an infinitesimal tension $-\delta P$, the exuded portion will return. If we suppose that the exuded portion is just sufficient to form a film wetting the outside of the pot, this film may be increased or reduced in thickness by an infinitesimal amount by an infinitesimal increase or decrease of pressure $+\delta P$ or $-\delta P$.

Now consider the pot filled with a solution. If we apply an infinitesimal pressure δP, no solvent passes through. In fact, we have in this case to apply a finite pressure P before exudation occurs. If we apply a pressure infinitesimally greater than P, say $P + \delta P$, exudation occurs, and if δP is sufficiently small, the exuded volume δV will also be small, and exudation will then cease. We then have the case of a solution under a finite pressure in equilibrium with a thin film of solvent under zero pressure. As δP tends to zero, the film becomes infinitesimally thin, but the osmotic pressure remains finite and equal to P. In this case the activity of the solvent seems apparent.

Mr. L. J. Hudleston: In his Paper Professor Porter gave it as his opinion that the molecules of a solute never reached the actual surface of the containing vessel or of the membrane, assuming that the "surface" theory of Laplace held here just the same as at the free surface, where a molecule near the surface is attracted inwards with the tremendous force of intermolecular attraction unbalanced by an equal outward pull, as, owing to the discontinuity at the surface, there is not an equal number of molecules on the outer side within the range of molecular attraction.

On this point I should like to ask if there are any data to indicate whether the molecules of a liquid come within the range of attraction of those of the containing vessel. If so, the above opinion might prove incorrect, as a molecule of solute at the surface of contact between the liquid and containing vessel, though attracted inwards by all the molecules (within range) of the solvent, would be attracted outwards by the molecules of the wall of the containing vessel, and the latter attraction might even be the greater, so tending to increase the concentration of the solute at the surface and hence, perhaps, offering an explanation of adsorption and similar surface effects, such as catalysis.

In the case of the membrane this suggestion seems even more likely to be true, as actual molecules of the solvent must lie in considerable concentration on the far side of the molecules of solute nearest the surface, thus neutralizing the Laplace effect. Hence it would seem that one must allow for the possibility of actual contact between the molecules of solute and membrane respectively, and therefore for their specific action on each other.

Mr. F. S. Spiers: A theory of osmotic pressure which does not take into account (1) the solvent, (2) the solute, and (3) the association between the two, does not seem to me to be entirely satisfactory.

I have always been accustomed to picture osmotic pressure as due to the loading of the solvent molecules by the solute. At any point in a pure liquid there must be an internal pressure due to local molecular bombardment, which is indicated by the Brownian movement. This of course is not the same as the internal pressure (of enormous magnitude) due to molecular attraction referred to by Sir Oliver Lodge.

The introduction of a solute leading to some kind of union between solute and solvent has the effect of loading a certain number of the solvent's molecules and rendering them less mobile. This will decrease the internal pressure due to molecular bombardment. It is this *reduction* in pressure which is the osmotic pressure.

At a surface separating the solute from the pure solvent the molecular bombardment will induce a higher pressure on the pure solvent side. Hence if a semi-permeable membrane be placed at such a surface, pure solvent will flow through it, until the pressures on the two sides are equal, or, alternatively, flow will be prevented if an external pressure equivalent to the osmotic pressure be exerted on the solute.

This conception appears to me to explain in a simple way (1) why pure solvent should flow through a semi-permeable membrane and (2) why the pressure necessary to prevent it is a measure of the osmotic pressure.

The conception of the solute loading the molecule of the solvent pictures directly the lowering of the vapour pressure and the raising of the boiling-point, and it also shows in a simple manner why there is a connection between these quantities and osmotic pressure.

Since writing the above, Professor Porter has drawn my attention to the fact that the theory stated here is substantially that put forward by Poynting.*

REPLIES COMMUNICATED BY THE AUTHORS.

Dr. F. Tinker.

In answer to Professor Philip's question as to how the view that a colloidal membrane is to be regarded as a separate phase in the osmotic system can be reconciled with its capillary structure, and why it is that a sugar molecule cannot enter a capillary having many times its own diameter : The conception of the copper ferrocyanide membrane as a separate phase, into which the solvent or solute can diffuse and be superficially condensed on to the surfaces of the colloidal particles, is in no wise incompatible with the view that it is also an aggregation of colloidal particles which enclose minute capillaries. I have shown † that these capillaries are completely under the control of surface forces, so that there are no free channels or capillaries as ordinarily understood connecting the opposite sides of the membrane. Any solvent or solute crossing a colloidal membrane of the copper ferrocyanide type is temporarily in the adsorbed condition, even though it may be travelling through capillaries. A distinction must therefore be drawn between membranes of the copper ferrocyanide type and membranes of the parchment type. The former have the properties of continuous media, owing to the fact that their pores are entirely within the range of molecular attraction, just as the "pores" of a liquid or solid are within that range ; the latter are essentially discontinuous in structure, since their capillaries possess a central core which lies outside the surface force range, and down which a solution can pass without change in concentration.

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* *Phil. Mag.*, **42**, 298.

† *Proc. Roy. Soc.*, A, vol. 92, p. 357 (1916).

Moisture diffuses through the pores of a copper ferrocyanide membrane in somewhat the same way as vapour would diffuse, only in a much more concentrated condition than in the vapour phase proper. Diffusion through a parchment membrane is a more complicated phenomenon ; on the one hand liquid unchanged in physical condition can flow down the central part of the pores ; on the other hand, the liquid which diffuses along the outer portion of the pores near to the walls of the capillaries is in the adsorbed condition, and has a different density, concentration, etc., from ordinary liquid. The one type of membrane merges into the other when the average capillary radius becomes equal to the range over which surface effects take place (10 to 20 $\mu\mu$).

The question as to why cane-sugar, for instance, cannot enter a capillary which has a diameter many times larger than the diameter of the sugar molecule can only be answered fully when we arrive at the ultimate explanation of why the concentration in surface films is different from that in the body of a solution. I am inclined to think that the mechanism of selective adsorption is ultimately that of the selective forces exerted by affinity. The affinity of water for sugar is in all probability greater than the affinity of water for itself ; with the result that a sugar molecule in a surface film is attracted by the body of the solution with a greater force than that exerted on the water molecules in the surface film. In consequence the sugar molecule is pulled inwards, just as a body immersed in water is pulled downwards if it is attracted by the earth with a greater force than water is attracted. If, in addition, the surface of the water is in contact with a colloid, such as copper ferrocyanide, which has a natural affinity for water, the conditions tending to displace the sugar molecule into the solution are still further intensified, so that it is quite easy to understand why the sugar molecule never reaches the surface of the colloid or enters the capillary at all.

In answer to the statement of Professor Porter that the membrane plays a secondary part only in osmotic phenomena, I agree that the direction of osmotic flow and the magnitude of osmotic pressure are determined ultimately by the conditions existing inside the pure solvent and solution respectively. But unfortunately these conditions are not yet fully known. In the meanwhile it is necessary to approach the problem as to what these conditions are from every angle ; and I believe that inasmuch as the pressure and concentration of the solvent inside the membrane are determined by these conditions, a study of the membrane and its relation to the solvent and solution respectively will assist materially in the solution of the problem. The most important point of my paper is that a vacuum is the simplest membrane there is ; and by employing it, the problem of the mechanism of osmosis reduces itself to a determination of what conditions inside liquids cause the vapour pressure of a solution to be less than that of a pure solvent, and why it is that placing a hydrostatic pressure on a liquid raises its vapour pressure. The solution of these latter problems has been sketched in the addendum to the Paper.

Mr. W. R. Bousfield.

A word may be added as to the suggestion made in the course of the discussion, that the figures given by me merely verify the thermodynamical relations, and that the introduction of the values of n serves no purpose. It may be pointed out—

1. That the values of the quantity n, which expresses the mols of combined water per mol of solute, are of primary importance in the theory of solutions.

2. That thermodynamics alone can throw no light whatever on this question.

3. That, as shown in the papers to which reference is made, we can estimate the values of n at different concentrations by reference to the variation of ionic velocity with dilution. Velocity depends directly upon size, and gives us an accurate measure of the amount of water which the ion carries in combination with it.

4. That the data for osmotic pressure, vapour pressure, and freezing-point lowering, when expressed in terms of the free water, all yield values of n which agree with those derived from measurements of ionic velocities.

This result necessarily verifies the thermodynamical relations, which is unfortunate in so far as it causes the true point to be missed. The real point is that what was shown by me in the case of freezing-point lowering some years ago also applies to osmotic pressures and vapour pressures, viz. that directly you correlate them, not to the *total* water h, but to the free water $h - n$, they can be mathematically expressed with the greatest simplicity and accuracy, in such a way as to give us a valuable means of checking the values of n derived in other ways.

It should be remembered that the primary purpose of my Paper was to throw light on the effect of the interaction between solvent and solute. The starting-point is the former Paper,* which gets the values of n from the ionic velocities and leads to the correlation of n with the freezing-point values by means of the relation

$$\Delta/F^1 = i/(h-n).$$

Thence follows the extension of the relation to osmotic pressure and vapour pressure. All this seems to be left untouched by any criticism.

The secondary object of the Paper was to show that the vapour pressure theory was in itself sufficient to account for the osmotic phenomena. Of this a mathematical proof was given which nobody has challenged. Then comes the question whether it is right to regard the solute as behaving as a gas within the solution. In answer to criticisms one more consideration may be adduced. If I put an open pot of sugar solution and another open pot of salt solution under an evacuated bell jar, there will be a transfer of water vapour until equilibrium is attained. The two solutions will arrive at osmotic equilibrium solely by equalization of vapour pressures. When osmotic equilibrium is determined by this simple condition, why resort to the unnecessary theory that the solutes in the two pots are behaving as gases in the two solutions? Why is it necessary to regard osmotic pressure as a sort of gas pressure? Professor Porter says "every molecule present (solute, vapour, liquid, etc.) has its osmotic pressure." No one would deny that every molecule present adds its quota to the pressure on the walls of the containing vessel. But the osmotic pressure of a *solution* is the pressure which must be applied to it to make its vapour pressure equal to that of the solvent. To speak of the "osmotic pressure" of each molecular species in the solution is to confuse ideas which must be kept clear if discussion is to be fruitful.

Professor Alfred W. Porter.

At the very front of my reply I will put a quotation from Mr. Spiers' communication: "A theory of osmotic pressure which does not take into account (1) the solvent, (2) the solute, and (3) the association between the two, does not seem to me to be entirely satisfactory." That is a statement to which we can all subscribe: probably it is the only one.

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* Loc. cit.

The discussion may be divided into several parts. One deals with the theory of osmotic pressure being for or against a "gas" theory. Another concerns itself with the meaning of a more or less empirical constant *b* in an extension of the gas theory. A third deals with the membrane. I will take these in the order given.

I. *General Theory.*

I must place Mr. Bousfield on the side of those upholding a gas theory; and as he has contributed a Paper as well as remarks in the discussion, it is only right that I should refer to these first. On the night of the discussion I had not had the opportunity of reading his Paper, and although I was vaguely acquainted with it from his previous publications, it was not possible for me to deal with it then.

The difference between van't Hoff's and Mr. Bousfield's theory is that while the former considers that the osmotic phenomena are a primary consequence of the presence of the solute, on Mr. Bousfield's theory the solute itself is very "inactive," but it produces a modification of hypothetical vapour molecules present in liquid water, and it is these "which are the real active things and which do the business." Now, in my opening remarks (which took the place of my printed paper, and which are not recorded) the first point on which I laid stress was that the work of Perrin and others on Brownian motion had showed, once for all, what had previously only been suspected, that the activity of even fairly large particles suspended in a liquid is precisely that given by the molecular theory of gases; or, in other words, that the molecular mass multiplied into the square of the velocity must be the same on the average for all particles at the same temperature. This must be true for the particles of both solvent and solute, of whatever degree of complexity. The massive ones move slowly, the light ones fast, but mV^2 is the same for them all. If by activity we mean "rate of moving about," then the light ones have the ascendancy; and rates of diffusion and, no doubt, rates of osmotic flow and evaporation are governed thereby. But in the equilibrium case it is this quantity mV^2 which is the important thing—the pressure of a gas is $\frac{1}{3}mV^2$, for example—and I would rather like to keep the term "activity" for this product, which is constant for all kinds at constant temperature, but increases with the temperature. Now, on the gas theory, for dilute solutions, it is this quantity upon which the osmotic pressure depends, and it is upon its sameness that the isotony of equimolecular solutions depends. If we have several molecular species present, in dilute amounts, in the same solution, then the osmotic pressure of each of these per molecule is the same. It is under the influence of this pressure that they diffuse. But to obtain external manifestation of the pressure itself, a selective membrane is needed which disturbs the social equality, stopping one kind and allowing all the rest through. The force per unit area which this membrane experiences is the difference of the pressures on the two sides. For infinitely dilute solutions only (and then only with reservations connected with molecular magnitudes) the permeating part may be considered to be the same on both sides, and the differential pressure is simply that due to the non-permeating part.

If Mr. Bousfield can find a membrane which will let sugar and "liquid" water through and will stop the "vapour" molecules, then the osmotic pressure experienced will be that due to the "vapour" molecules. *But that is not the kind of membrane that Morse and Berkeley have used.*

The van't Hoff school does not arbitrarily ignore the osmotic pressure of any molecular species present; on the contrary, it recognizes that every molecule present (solute, "vapour," "liquid," etc.) has its osmotic pressure. It is Mr. Bousfield who ignores the direct effect of the one molecular species which we know is there (the solute), and takes into account an *assumed* modification of another molecular species ("vapour") which he *assumes* to be there. The reason given for neglecting the sugar is that it is very "inactive," since it has no vapour pressure. Lord Berkeley's example (given in the discussion) is sufficient evidence to the erroneousness of taking the vapour pressure as the measure of the pressures in the solution.

A great deal of the pother is the result of the equality of action and reaction. One may discuss the forces acting *on* the water, or *on* the solution, or *on* the solute, or *on* the membrane; or we may investigate the forces exerted *by* each of these. The osmotic experimentalist examines the force exerted on the membrane by taking it as equal to the difference of the forces exerted on its two sides. This force acts outwardly, i.e. from the solution towards the solvent. This is also the direction of the pressure arising from the molecular bombardment due to the solute.

I wonder if there is anything subtle behind Mr. Bousfield's questions relative to the pressure on his glass tumbler (p. 40), or whether he is merely a little hazy in regard to the mechanics of Laplace's attraction. I might employ the *argumentum ad hominem* and ask him the same question in regard to the pressure due to his "vapour" molecules. But I counter his queries with another. How is it that the pressure inside a cylinder of compressed gas can be so very high while outside it is only atmospheric? It is because there is an intervening layer of steel molecules, held together by their mutual attractions, whose combined effect balances the excess pressure. The molecules of a liquid are similarly held together by attractive forces which permit a difference of pressure of 10 or 20 thousand atmospheres between inside and outside. The problem is a very familiar one and I have nothing new to add to it here.

In my opening remarks I emphasized that van't Hoff's gas theory is the *only one* from which the value of the osmotic pressure has been calculated *a priori*. This cannot be done from Mr. Bousfield's, because he is obliged to introduce his *ad hoc* assumption in regard to the modifying influence of the solute on the "vapour" molecules, so I cannot withdraw van't Hoff's theory in favour of his. But Dr. Shorter takes up the challenge and presents a new theory. He says, "We must start from some law whose kinetic explanation is immediately evident," and he finishes his exposition by saying, "It is true that the above exposition does not provide a direct kinetic explanation of the 'gas' law"! What more could have been asked for in the way of admission!

Without the aid of thermodynamics Dr. Shorter gets as far as a proof of Henry's law for dilute solutions. He then introduces Duhem-Margules' law, which is purely thermodynamical, and thus obtains Raoult's law, from which the gas law can be deduced—again by thermodynamics.

Now, of course, I did not mean to throw discredit upon those thermodynamical relations by means of which osmotic pressure has been calculated from vapour pressures, freezing-points, etc. These relations are independent of any mechanical theory. I cannot think that my statement will have been generally misinterpreted.

What we may deduce from Dr. Shorter's new "theory" seems to me to be this. Even if we start from a law such as Henry's law, which he puts on a simple and logical mechanical basis—a law expressible in terms of a constant k, the value of which depends upon the forces between solute and solvent (as he carefully points out); yet, when the next step is taken, this factor k (depending upon the forces between solute and solvent) automatically disappears from the result, because the Duhem-Margules equation is a logarithmic differential one and $d \log kc = d \log c$. Hence the final conclusion (i.e. the gas law) is *independent of the only factor which involves the forces between solute and solvent.* This is a very striking and instructive fact; for it shows that Dr. Shorter must be wrong when he emphasizes "the fact that intermolecular forces play a part even in dilute solutions." Even if you deliberately start with a phenomenon which involves these forces, they automatically disappear from the value finally obtained for the osmotic pressure.

And therefore, when in Part I of his contribution to the discussion (p. 43) he obtains a different result by means of an application of Clausius' virial theorem, his statements require to be looked into very carefully. His demonstration does not seem to me to be satisfactory. No application of the virial theorem can possibly be of any value unless you introduce the condition that the solution and pure solvent are to be in osmotic equilibrium with one another. Dr. Shorter does not do this. Of course, unless this condition is attended to, the external pressure may be whatever you please. He does not mention the solvent—even that in the solution; so I take it that he assumes it to be undisturbed by the presence of the solute. If you reckon only the direct pressure of the sugar which reaches the external surface, no one expects this to be equal to the osmotic pressure—because of the mutual forces. But when mutual forces are taken into account it must not be forgotten that they are mutual; and in so far as the sugar is pulled back in the surface layer, that layer itself is pushed forward and thus serves as a transmitter of pressure. It is in this way that a personal blow is transmitted through an intervening layer. I do not see how to rectify Dr. Shorter's expressions, though I have made many attempts during the last twelve months to obtain a correct expression. The doubtful step is how, properly, to introduce the equilibrium condition. But when mutual forces are ignored I think the statements made in my Paper are substantially correct. Dr. Shorter thinks that the gas law is a matter of pure coincidence when terms arising from mutual forces and free space cancel. Surely this is to put a tremendous strain upon one's credulity! The case he cites, in illustration, of the adventitious cancellation of the a and b effects in a real gas, only holds good at *one* pressure for any given temperature, and this is different for different substances. The cancellation in the osmotic case must hold for all substances in the dilute state at all temperatures —as thermodynamics shows.

This reply is applicable in part to the similar objections raised by Professor Moore; but a few more words are necessary in connection with his illustration from mixed gases. In order to calculate the external pressure on mixed gases at high pressures, all three of his complications must undoubtedly be taken into account. The van der Waals school write the characteristic equation in some such form as

$$p + \frac{n_1^2 a_1^2 + 2n_1 n_2 a_1 a_2 + n_2^2 a_2^2}{V^2} = \frac{RT}{V - n_1 b_1 - n_2 b_2},$$

where p is the external pressure. With regard to this equation, it must first be mentioned that it tells one nothing about the *partial* pressure of either constituent, for the equation is not linear, and therefore the additive law does not hold. Nor is it the partial pressure of the sugar of which we are in quest (as was said above). Professor Moore's considerations, equally with those of Dr. Shorter, fail to introduce the question of equilibrium. If we were able suddenly to remove the sugar from the solution at pressure p, the solvent remaining would not, in general, be at the equilibrium pressure p_0. This is another way of putting it which may help to reveal where possible pitfalls lie.

Professor Findlay leans towards Tammann's views as to the origin of osmotic pressure, which he attributes to change in the Laplace internal pressure. Now, undoubtedly, since all the forces in a liquid at rest must form an equilibrium system, there must be a numerical equality between those arising kinetically and those which have a static origin, and if we could see clearly enough, it must be possible to use either one set or the other set of forces. There are two ends to every stick. But unfortunately those who have caught hold of the intrinsic pressure end have not managed to do anything satisfactory with it. Van't Hoff caught hold of the other end and used it successfully.

Tammann and Horiba find that the intrinsic pressure of the solvent increases with increase in concentration of the solution. What Tammann really found was the total increase in intrinsic pressure ; Horiba, I fancy, assumes the additive law, and divides the increase between solvent and solute. Now, is it not remarkable that, although the intrinsic pressure is increased, the total internal pressure must be *still further* increased by the amount P by increasing the external pressure before the solution is in osmotic equilibrium with some of the original solvent ? Looking at the question from the point of view of intrinsic pressure of the solvent alone, is there any mechanical reason for this ? Would one not expect that the external pressure would need to be *diminished* to bring about equilibrium ? Surely this indicates that Tammann's method is essentially unsound.

The remarks that I have made about the failure of the additive law apply also to the theoretic part of Dr. Tinker's Paper—especially to the addendum, where he becomes more explicit. There is so much in this and in the *Philosophical Magazine* paper to which he alludes (May, 1917), to which I must raise objection, that I postpone a full criticism to another place. There are one or two things I will mention here. Dieterici's equation is a very unsafe guide for this problem, because it breaks down completely in the liquid phase, although it is very much superior to van der Waals' equation in the gaseous region—at least it becomes so if the power of T in the index is increased to about 3/2, but not otherwise.

I cannot follow the derivation of Raoult's law on p. 22. It is necessary for me to mention that Dr. Tinker (in his *Phil. Mag.* paper) assumes that the internal pressure is given by RT/(free space per mol). I have no quarrel with this assumption as a provisional one, though, of course, it cannot have a rigorous validity. (I have used it myself in connection with a gas equation I am developing.) As our symbols are at variance with one another, let us put I for the internal pressure. Then for N mols of pure solvent we have

$$I_0 = \frac{NRT}{V_0 - Nb_0}$$

when they occupy a volume V_0.

For n mols of pure solute,

$$I = \frac{nRT}{V - nb}.$$

If these are mixed we have (assuming b and b_0 to be constants)

$$I' = \frac{(N + n)\,RT}{V' - Nb_0 - nb}.$$

If for simplicity we keep to the case of no contraction,

$$V' = V + V_0.$$

It is easy to deduce that

$$\frac{N+n}{I'}=\frac{N}{I_0}+\frac{n}{I}$$

or if we put x for the molar fraction of the solute

$$\frac{1}{I'}=\frac{1-x}{I_0}+\frac{x}{I}.$$

This is the equation which I would substitute for a somewhat similar one of Dr. Tinker's, in which the values of I are in the numerator instead of the denominator. (It is a misleadingly simple equation, because the values of I are also functions of x.) In none of this, however, is there any justification for taking

$$I'/I=\frac{N+n}{N},$$

nor do I know of any argument or experiment which leads us to expect this ratio for the *internal* pressures, although a similar one is known as Raoult's law for vapour pressures. I would like to see his foot-note on p. 23 expanded; it seems to me to be wrong. Assuming no internal work done, the second law shows that $p = Tf(v)$; it is the gas theory that gives the relation $pv = RT$. Secondly, it is Henry's law that is required in addition. However, I may misunderstand him. I hope to return to a criticism of Dr. Tinker's *Philosophical Magazine* paper in the appropriate place.

Dr. van Laar is impressed by the connection between osmotics and diffusion. This connection is universally recognized. But the gas-theorist prefers to deduce diffusion constants from osmotics. The reverse process is full of difficulties, and suffers moreover from the defect that we are only concerned with the properties of the solution which obtain when the diffusion is over. Moreover, I doubt whether the transfusion of the solvent through the membrane is diffusion at all, though the ultimate mixing of the transformed liquid with the solution is undoubtedly diffusional.

Although his logarithmic law may be correct for the case of very dilute solutions—in which case we may as well write x instead of $-\log(1-x)$—there is no guarantee that it is correct to even the second order of small quantities; so that instead of $-\log(1-x)-ax^2$ we may equally well write $x+a'x^2$, where the second-order term is an *empirical* attempt to represent the deviation from proportionality to the concentration. Moreover, it is not clear where the factor RT springs from. It may be taken for granted *always* (and it is very useful to remember) that when this factor appears *the gas law has been made use of either directly or indirectly. Thermodynamics cannot introduce it.*

In this section of the subject I am most attracted by the communicated remarks of Lieutenant Partington, and I concur entirely with them.

Lord Berkeley also brings forward a very conclusive case against the steam theory put forward by Mr. Bousfield. Vapour pressure is not a measure of activity in solution. If it were, the most volatile materials might be expected to have the greatest osmotic pressure. Lord Berkeley has difficulties in seeing how diffusion is brought about (on the vapour theory) in the example he gives. I concur (as the learned judges say).

II. *Hydration Numbers.*

Both Dr. Senter and Professor Lowry oppose the hydration numbers I calculate from Morse's values. Both base their opposition on the law of mass action, but in rather different ways. Dr. Senter follows Nernst in assuming an equilibrium equation of the simple type

$$S+nH_2O \rightleftharpoons S(H_2O)_n,$$

or, as we may write it,

$$A + nB \rightleftarrows C,$$

and asserts that in relatively dilute solution "the active mass of the water on the left-hand side of the equation scarcely varies with further dilution." I agree with this statement; I do not agree with the deduction from it. For the equation of the above type implies an equilibrium constant of the type

$$\frac{AB^n}{C}.$$

Provided that n is small, i.e. provided we are dealing with a di- or tri-molecular reaction, undoubtedly Dr. Senter's conclusions would be justified. But we are dealing with a case in which n is of the order of 50 or 100, that is, with quinquagesimal or higher reactions, and in such cases a minute reduction in B causes a very considerable change in C and A. For example, with $n = 100$ a reduction of B by 1 per cent. would reduce the ratio C/A to an eighth part of its first value. I do not consider that vapour pressures are a safe guide to the values of the active mass, especially when the active mass is needed with such great accuracy as in this case; but as this is only a side issue, I will not stop to give reasons. Yet I must add that I do not think that any such simple reaction equation as that given above can be expected to be adequate. It assumes that the molecular species are of three types only—water, sugar, and a *definite* compound formed from them. But this will not be the case. There will be hydrates of many degrees of complexity—any complexity, in fact, from the anhydrous sugar up to a value of hydration of (say) 100 or more. In such a case the equation becomes

$$A + nB = n_1C_1 + n_2C_2 + n_3C_3 + \text{etc.},$$

with the condition $n = n_1a_1 + n_2a_2 + n_3a_3 + \text{etc.}$, and the flexibility of such an equation is so great that it can be made to fit *almost* any experimental data.

Dr. Lowry's objection is essentially different from Dr. Senter's, inasmuch as he finds that, with my numbers, the *total* hydration diminishes, although the product of the amounts of the simple reactants has increased. Certainly, this result is contrary to the law of mass action; and, certainly, the numbers 53 and 16 quoted by Dr. Lowry break this law. I hardly expected them to be accepted so rigidly as this, however. Remember that instead of 53 (from Morse) I also give 15 (from Berkeley), and I do not tie myself down to either. I give merely what the experimental data require if interpreted according to a particular theory. Until the discrepancy between these experimental data is cleared up these hydration numbers can only be accepted in the rough. But the matter is not quite as Lowry's calculations would indicate, for he has forgotten to allow for the *variation of volume*. I give below values calculated rigorously from the law of mass action to illustrate my point:—

Weight Normal Concentration. $1{,}000\frac{n}{M}$	Vol. Normal Concentrations.		Hydration Numbers deduced from	
	Sugar.	Water.	Morse.	Mass Action.
·1	·098	54·44	53	53
·2	·192	53·33	15·8	23·3
·3	·282	52·17	10·3	12·0
·4	·369	51·25	7·7	7·7

The last column of numbers would violate the law as employed by Dr. Lowry. But with regard to the high numbers, although "I do not know of any argument which makes them impossible," no assertion is made as to their *probability*. I do assert this of the values obtained from Berkeley's data.

Mr. Bousfield considers that the high hydration numbers are made impossible by evidence supplied by the viscosity of sugar solutions. Do we know enough, however, about the viscosity of solutions to warrant resting too much upon this evidence? It is true that Einstein in 1906 proved that for suspended particles, sparsely enough strewn through a liquid, the increase of viscosity due to their presence, i.e. $(\eta - \eta_0)/\eta_0$, should be given by

$$a \times \frac{\text{Total volume of suspensoid}}{\text{Total volume of liquid}},$$

in which formula he first put $a = 1$, but afterwards (in 1910) corrected it to 2·5. [Dr. G. B. Jeffery, working with me, had previously, but at practically the same time, discovered the mistake in the constant by an independent mode of calculation.] Bancelin found experimentally the factor 2·9, while Humphrey and Hatschek, working with low rates of shear, find as high as 18 for starch grains in equally dense mixtures of carbontetrachloride and toluene. Taking the numbers of Grüneisen, I calculate $a = 4·9$ for the ·2 normal solution and $a = 4·3$ for the ·05 normal solution, assuming the sugar molecule to be of the same size as a gram molecule of the solid. The figures are in concordance with a hydration number about 10; so that, taking this evidence, even Berkeley's values are too high. But it must not be forgotten that the theory worked out by Einstein assumes that the suspensoid is in the form of rigid spheres. Is it safe to rest too much upon it, when applied to molecules carrying with them molecules of water which are in a perpetual state of transition—sometimes moving with the sugar, sometimes swept off, due to the action of the rest of the water?

Latent Heats of Dilution.—The real test will be forthcoming when the heats of dilution are measured in the same regions as those about which the main doubt exists; these determinations are in progress. Lord Berkeley asks for information of the possible accuracy of this method. The latent heats can themselves be determined to about one part in 150. But it must be observed that they are proportional to the rate of increase with temperature of P/T. Now, P/T would be a constant if the gas law held; in reality it varies by about 10 per cent., hence the determination of P can be made to about 1 part in 1,500.

Dr. Senter points out that the deviations from the gas law have previously been attributed to hydration by Nernst, Bredig, Sackur, etc. I was aware of that part of Sackur's work which he records in his *Thermochemie u. Thermodynamik.* I had previously (in 1907 or 1908) done the same thing with Berkeley's numbers. The only novelty that I think I can claim is in so far as I test the much more complete set of values of osmotic pressure now available and work out in detail the variation of hydration that would be necessary to account precisely for these experimental results. It is not too much to say that Bredig and Nernst had *no* exact data by which to test any theory.

Mr. Bousfield claims superiority for the hydration numbers he gives on p. 34 to those which I give on p. 12 because the observed and calculated values are "not only equally close, but they are even closer than mine." He appears not to have noticed that I give the table on p. 12 merely to reject it as not doing complete justice to the accuracy of Berkeley's experiments; and I replace it by another on p. 13 which necessarily fits *exactly*, instead of only approximately, as Mr. Bousfield's does. In fact, although Mr. Bousfield has allowed himself to treat his *n* as variable with concentration, the result is scarcely at all better than what could have been obtained if he had kept *n* constant. The sum of the differences between observed and calculated values (without respect of sign) is 67 in his case and 87 in my approximate table (with constant *n*). It is not worth while to introduce variability into *n* in order to effect this slight improvement.

I cannot agree that *n* is anything but an adjustable quantity which has to be selected to fit experimental values. If the values taken from freezing-points fit osmotic pressures (or *vice versa*), it indicates a relationship between these phenomena, but does not alter the essential character of *n*. The existence of this relationship is also indicated by thermodynamics. The similarity in the value of *n* obtained from different phenomena was shown by Callendar (1908), and I believe had also been shown by H. C. Jones. Mr. Bousfield's calculation of the osmotic pressure is really made from the formula—

$$\frac{P}{R'T} = \frac{\Delta}{F'}$$

and he need never have calculated *i*, *h*, and *n* separately at all. Since this equation is derivable thermodynamically, it is independent of any theory of the mechanism of osmotic phenomena. In this respect it is on a par with Lord Berkeley's calculations from vapour pressures for even concentrated solutions. (I hope no one has been charging me with having forgotten these eminently successful calculations.) So I must reaffirm that the gas theory of that mechanism is the only one from which osmotic values have been satisfactorily calculated.

Of course, Mr. Bousfield is quite justified in calculating the value of *n*. But if he calculates it from the experimental values of osmotic pressure he will find a much higher value for dilute solutions than that which he has deduced from freezing-points—in fact, he will find practically my values. Again, he seems to have overlooked the table I gave for Berkeley's concentrated solutions.

III. *The Membrane.*

I am very interested in the properties of actual membranes, though I am certain they will not throw any light upon osmotic pressure. They are needed to explain osmosis—a very different thing, as Professor Findlay points out—and they form a very proper subject of study. And it must not be forgotten that membranes are of many grades, ranging from the absolutely impermeable, such as glass or steel, to the absolutely permeable, such as the piers of a bridge. How is it that certain membranes stop certain substances entirely, letting others through? Bearing in mind that one such membrane is the free surface of the solution, my own tendency would be to take it as an index of the true answer to this question and to say that there was negative adsorption of sugar at that surface, or, more explicitly, the attraction between sugar and water is so great that in the surface film the motion of all the sugar molecules is reversed before they reach the outside, although a proportion of the water molecules still have velocity left to escape and form vapour. Does any one dispute that this is the action at the free surface by which its semi-permeability is brought about? I would expect something similar at a solid surface, though since there will be attraction between the solid and sugar, the apparent repulsion of the sugar may be less (as Mr. Hudleston points out) and may even become a resultant attraction. There would be negative adsorption of sugar and positive adsorption of water. So far I think this is in agreement with Dr. Tinker's view. Beyond this point I am more doubtful of his views, in spite of some communication that has taken place between us since. In an ordinary copper ferrocyanide membrane in equilibrium with solution and pure solvent on its two sides, there must be a gradient of pressure, it being p on the solution side and p_0 on the solvent side. The pressure difference between the faces of any elementary layer is balanced by the elastic forces in the membrane. Now, under certain circumstances the adsorption of water increases with the pressure. I am not sure about these circumstances, because from the foot-note on p. 18 I would gather that the ferrocyanide at high pressure would adsorb the same as from pure water, whereas the plain interpretation of the text seems to be that under the circumstances in which an osmotic membrane finds itself, the adsorption of water from the solution does increase on the high-pressure side until it becomes the same as the adsorption from pure water at low pressure, and that the concentration of water in the membrane becomes uniform when osmotic flow ceases. [I feel sure this last is what Dr. Tinker means, though it seems to be at variance with the foot-note. Is there not some confusion in regard to the distribution of stress in a membrane ?] Now, I dispute the assumption of this uniformity of concentration which is at the back of all Dr. Tinker's writings. There is a gradient of pressure in the membrane, and the general effect of such a gradient is a gradient of concentration. Witness the gradient of concentration with height in a gravitating column of solution. The following simple proof is worth giving here in order to emphasize the point. In the figure A and B are semi-permeable membranes. The other symbols explain themselves. We have—

$$\frac{dp}{dh} = -\frac{g}{\sigma} \quad \frac{dp_0}{dh} = -\frac{g}{u},$$

whence—

$$\frac{dp}{dp_0} = \frac{dP}{dp_0} + 1 = +\frac{u}{\sigma},$$

where P is osmotic pressure. But P is a function both of concentration, c, and the height. Hence—

$$\frac{dP}{dp_0} = \frac{\partial P}{\partial p_0} + \frac{\partial P}{\partial c}\frac{dc}{dh}\frac{dh}{dp_0},$$

and by a familiar relation—

$$\frac{\partial P}{\partial p_0} = \frac{u - s}{s},$$

where s is the shrinkage.* Moreover, approximately

$$\frac{\partial P}{\partial c} = RT, \text{ or more exactly } \frac{RT}{(1 - cb)^2}.$$

Hence—

$$\left[\frac{u - \sigma}{\sigma} - \frac{u - s}{s}\right] = -\frac{RT}{(1 - cb)^2}\frac{u}{g}\cdot\frac{dc}{dh},$$

or—

$$\frac{dc}{dh} = -g\left(\frac{1}{\sigma} - \frac{1}{s}\right)\frac{(1 - cb)^2}{RT}.$$

Since, in general, σ is less than s, there is a decrease of concentration as the pressure diminishes. I expect, in the same way, a difference of concentration of the water in the semi-permeable material in which it is dissolved in passing from the solution side to the side of pure water. It would seem that the equality of concentration which Dr. Tinker expects cannot, in general, obtain. This is the objection which I have always felt against those indirect methods of determining osmotic pressure which rely upon measurements of the variation of pressure required to produce the same absorption of water from a solution as takes place from pure water at ordinary pressure.

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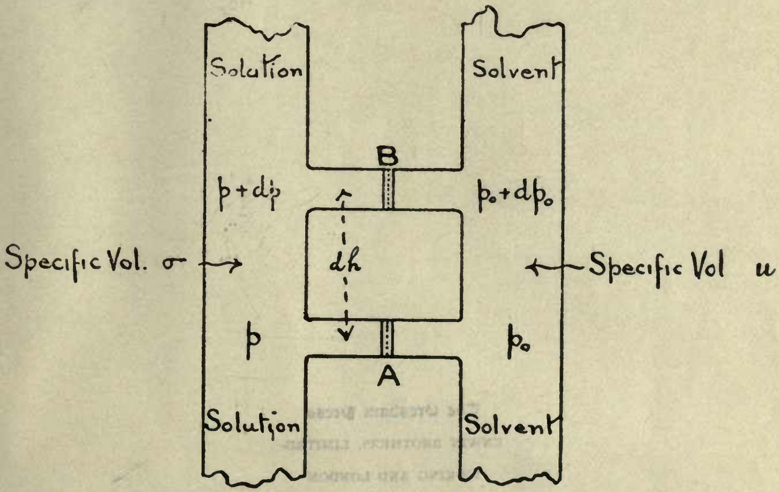
* Porter, *Roy. Soc. Proc.*, A, 1907, p. 522.

The recognition of the rôle of selective absorption in semi-permeability is quite old, as Professor Philip points out. It is as old as Graham; it was given by Nernst[*] as a method of determining osmotic pressures.



More recently it has been used by Professor Trouton toward the same end in the case of a sugar solution;[†] and in that case, at any rate, the method yielded a value close to Lord Berkeley's directly determined value, indicating that the correction for the gradient of concentration may not be very large.

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[*] Nernst, *Zeitschr. physik Chem.*, 6, 16 (1890).

[†] Trouton, *Roy. Soc. Proc.*, A, vol. 86, p. 149 (1912).

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